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Heterodoxy in Fast Pyrolysis of Biomass

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Abstract

As the field of fast pyrolysis has matured, it has been accompanied by a kind of orthodoxy in its practice. Among these orthodoxies are the following: (1) oxygen should be excluded from the pyrolysis process; (2) little sugar is produced during pyrolysis; and (3) the major product of pyrolysis is a low-value emulsion in water. Adherence to these tenets is an impediment to the commercial development of fast pyrolysis. Over the past 15 years, research at Iowa State University's Bioeconomy Institute has challenged these tenets with what might be called heterodoxy in the science and engineering of fast pyrolysis: adding oxygen, producing sugars, and fractionating bio-oil into valorized products. This paper reviews these new approaches to pyrolysis and concludes with an outlook for further developing them.

Keywords

Fast pyrolysis, biomass, bio-oil recovery, autothermal, anhydrosugars, phenolic oil, pretreatment, process intensification

Disciplines

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Heterodoxy in Fast Pyrolysis of Biomass

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Fast pyrolysis, biomass, bio-oil recovery, autothermal, anhydrosugars, phenolic oil, pretreatment, process intensification

ABSTRACT

As the field of fast pyrolysis has matured, it has been accompanied by a kind of orthodoxy in its practice. Among these orthodoxies are: (1) oxygen should be excluded from the pyrolysis process; (2) little sugar is produced during pyrolysis; and (3) the major product of pyrolysis is a low-value emulsion in water. Adherence to these tenets is an impediment to the commercial development of fast pyrolysis. Over the past fifteen years, research at Iowa State University's Bioeconomy Institute has challenged these tenets with what might be called heterodoxy in the science and engineering of fast pyrolysis: adding oxygen, producing sugars, and fractionating bio-oil into valorized products. This paper reviews these new approaches to pyrolysis and concludes with an outlook for further developing them.

INTRODUCTION

The development of fast pyrolysis for thermochemically processing biomass dates to the early 1980's. As might be expected for a forty-year-old technology, maturity has brought with it a kind

of orthodoxy regarding the practice of fast pyrolysis. Among these tenets are: (1) oxygen should be excluded from the pyrolysis process to avoid oxidative degradation of bio-oil; (2) thermal depolymerization of lignocellulosic biomass produces very little sugar; and (3) the major product of pyrolysis is a complex and low-value emulsion of lignin-derived oligomers in an aqueous phase of mostly light oxygenated compounds. In fact, adherence to these tenets is an impediment to the commercial development of fast pyrolysis. Over the past fifteen years, research at Iowa State University's Bioeconomy Institute has challenged these tenets with what might be called heterodoxy in the science and engineering of fast pyrolysis.

Exclusion of oxygen appears to be eminently reasonable to prevent oxidation of condensable organic vapors to non-condensable gases. An often-overlooked advantage of adding a small amount of oxygen is the possibility that the exothermic energy release from partial oxidation of the products of pyrolysis will provide the enthalpy for pyrolysis. Such an autothermal process eliminates the need for heat transfer into the reactor, with several important advantages including simpler reactor design, process intensification, and improved scalability.

The conventional view that sugars are a minor constituent of the products of pyrolysis arises from the presence of alkali and alkaline earth metals in biomass that catalyze pyranose ring fragmentation in cellulose and hemicellulose. While some researchers advocate washing of these cations from the biomass prior to pyrolysis to enhance sugar yield, we find that in-situ passivation of this catalytic activity is a simpler and more cost-effective approach to enhancing pyrolytic sugar yields from pyrolysis of biomass.

As an alternative to producing whole bio-oil, the condensable vapors of pyrolysis can be recovered as stage fractions according to boiling point. These fractions are further separated into

anhydrosugars, phenolic oil, and acetate for which the sum of their parts is of greater value than the whole bio-oil.

These three heterodoxies were developed independently but synergies among them have emerged. This paper reviews the development of autothermal pyrolysis, enhancement of pyrolytic sugar production, and bio-oil fraction to recover and purify sugars, concluding with an outlook for further developing these technologies.

AUTOTHERMAL PYROLYSIS

Autothermal pyrolysis aspires to replace heat transfer with partial oxidation of pyrolysis products to provide the energy required to drive endothermic pyrolysis reactions. However, pyrolysis, as conventionally defined, is the thermal decomposition of biomass or other carbonaceous solids in the absence of oxygen, a definition embraced by the author several years ago in writing a textbook on biorenewables resources.¹ The exclusion of oxygen seems eminently reasonable, with the expectation that the vapor products of pyrolysis would readily react with oxygen at typical pyrolysis temperatures of 400°-600°C, degrading the yield of bio-oil. However, the scientific literature was silent on the subject until a few years ago. Combustion of pyrolysis vapors at temperatures above 1200°C and equivalence ratios exceeding 100% has been extensively studied with the goal of completely oxidizing the vapors to carbon dioxide (CO₂) and water (H₂O).² Gasification of pyrolysis vapors at similar temperatures but equivalence ratios closer to 20% have also been investigated with the goal of producing flammable gas mixtures consisting primarily of carbon monoxide (CO) and hydrogen (H₂).³

The first paper on the effect of oxygen on pyrolysis at temperatures and equivalence ratios much lower than typical of combustion and gasification appears to be that of Butt in 2006,⁴ who

found a positive effect of low oxygen concentrations on yields of phenolic monomers when pyrolyzing pine. Eight years later, our research group found that low concentrations of oxygen (0.5 – 1.0%) in a continuous fluidized bed pyrolyzer, representing equivalence ratios of 0.03 to 0.06, increased the yield of hydrolyzable sugars (see Figure 1) and phenolic monomers from pyrolysis of red oak.⁵ Furthermore, BET surface area of biochar increased with oxygen concentration, increasing almost fifty-fold when oxygen concentration reached 4.2%, making the biochar more attractive as sorbent. As would be expected, partial oxidation increased production of water and non-condensable gases, especially carbon dioxide, which detract from the advantages accrued from admitting oxygen to a pyrolyzer. Similar results were reported by Jiang et al.⁶ several years later.

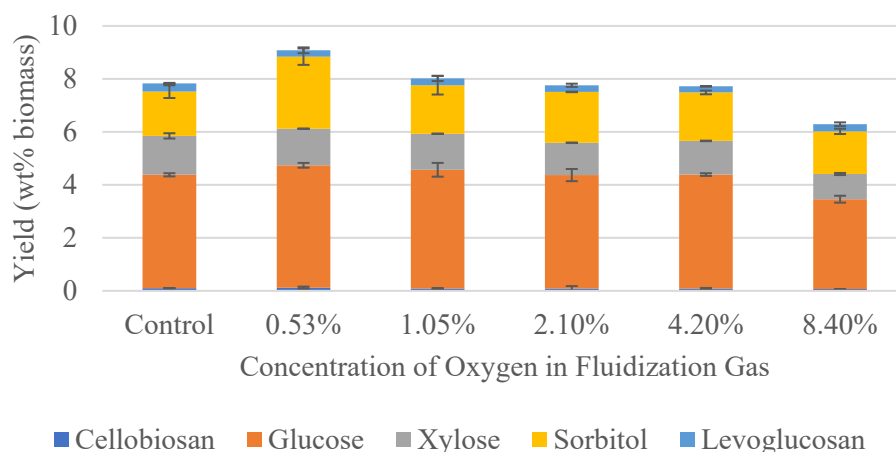


Figure 1. Effect of oxygen concentration in fluidization gas on sugar yields (monosaccharides from hydrolysis of sugars in bio-oil; chart prepared from tabulated data in Kim et al.⁵).

In retrospect, it is surprising that these early studies on “partial oxidative pyrolysis” did not immediately encourage development of autothermal pyrolysis. A simple thermodynamic analysis demonstrates how little oxygen is required to support autothermal operation of a biomass pyrolyzer. The fractional consumption of chemical energy in the biomass, f_E , to support autothermal operation of an adiabatic pyrolyzer can be estimated by:

$$f_E = \frac{\Delta H_{PYR}}{\Delta H_{LHV}} \quad (1)$$

where ΔH_{PYR} is the enthalpy for pyrolysis (that is, the energy to raise dry, solid reactant from standard conditions to pyrolysis temperature and chemically transform the reactant into volatilized products) and ΔH_{LHV} is the lower heating value of the reactant (that is, the energy released upon oxidizing the reactant to gaseous CO_2 and H_2O). Since the amount of energy released from oxidizing a given type of biomass is proportional to amount of oxygen consumed, the equivalence ratio required to achieve autothermal operation is approximately equal to f_E . Table 1 estimates the equivalence ratio for autothermal pyrolysis for several kinds of biomass based on the assumption of partial oxidation of some fraction of the biomass to CO_2 and H_2O). Enthalpies for pyrolysis are from measurements performed in our laboratory several years ago⁷ while the lower heating values were estimated from higher heating values obtained from several sources. From this analysis, we should expect equivalence ratios on the order of 0.08 to achieve autothermal operation in an adiabatic pyrolyzer although additional oxygen would be required to overcome parasitic heat losses in real reactors.

Table 1. Equivalence ratios estimated from thermodynamic data to support autothermal pyrolysis of different kinds of biomass (enthalpies for pyrolysis from Reference 7; lower heating values estimated by correcting higher heating values from various sources).

Biomass	ΔH_{LHV} (MJ/kg)	ΔH_{PYR} (MJ/kg)	Estimated Equivalence Ratio for Autothermal Pyrolysis
Red oak	19.3	1.46	0.076
Oat hulls	18.1	0.78	0.043
Pine	21.2	1.64	0.077
Corn stover	16.8	1.35	0.080

In fact, charcoal kilns dating back thousands of years are probably the first example of autothermal processing although these slow pyrolyzers were intent on producing charcoal rather than bio-oil.⁸ The combination of exothermic charring reactions and partial oxidation of the products of kilning provided the energy to drive the endothermic reactions of cracking and

devolatilization to produce charcoal. Air or oxygen-blown gasifiers are also autothermal processes⁹ although these ideally attain chemical equilibrium, producing a flammable gas mixture whereas fast pyrolysis is deliberately operated far from equilibrium to produce primarily liquid products.

The first mention of autothermal pyrolysis in the scientific literature appears to be a 1995 study by Wey et al.¹⁰ in Taiwan on the thermal depolymerization of waste tires in a fluidized bed reactor. Over the next three years, this group published additional papers on “oxidative pyrolysis” of solid wastes (scrap tires and polyethylene).^{11,12} These papers did not garner much attention, possibly because of the high equivalence ratios investigated (indeed, the authors spoke of “pseudo-incineration”) and reported the counter-intuitive result of reaction temperature dropping as equivalence ratio increased (possibly because equivalence ratio was increased by increasing air flow rate rather than decreasing the feed rate of the waste material). No attempt was made to control reaction temperature or measure energy flows.

The next report on autothermal pyrolysis did not occur until early 2012. For over thirty years, Olazar and colleagues at the University of the Basque Country have advanced the use of conical spouted beds in the pyrolysis and gasification of biomass and wastes.¹³ Recognizing the challenges of providing thermal energy to these reactors as they were scaled up, they proposed mixing air and nitrogen to introduce various levels of oxygen into the fluidizing gas and achieve autothermal operation of a spouted bed pyrolyzer vs conventional pyrolysis in nitrogen or other inert gas as fluidization agent.¹⁴ For their experiments, a small conical spouted bed reactor (maximum diameter of 12.3 cm) was preheated close to the desired pyrolysis temperature of 500°C before shutting off power to the electrical heaters and feeding 2 g min⁻¹ of pinewood and sufficient air-nitrogen mixture to operate at gas velocity 20% higher than the minimum spouting velocity (about

10.5 L min⁻¹). Rather than adjusting upward the equivalence ratio until the desired pyrolysis temperature was achieved, equivalence ratio was set and the preheat temperature of the entering gas adjusted to achieve the desired pyrolysis temperature. Two equivalence ratios were evaluated: 0.15 (requiring a gas preheat temperature of 470°C) and 0.25 (requiring a gas preheat temperature of 420°C). These are much higher equivalence ratios than anticipated from the analysis shown in Table 1 and are closer to what would be employed in autothermal gasification. Although not explicitly addressed in the paper, this likely reflects the need for additional energy release to overcome parasitic heat losses from this small reactor. Bio-oil yield (dry basis) from biomass dropped from 50.0 wt% under nitrogen-blown pyrolysis to 48.3 wt% and 46.9 wt% for equivalence ratios of 0.15 and 0.25, respectively, while char yield decreased by 25% and 42%, respectively. Most of the organic loss to the bio-oil yield was saccharides and phenolic compounds.

In 2013 Mesa-Pérez reported on the “fast oxidative pyrolysis” of sugar cane straw in a pilot plant at the University of Campinas in Brazil. The reactor was a 41.7 cm diameter fluidized bed with air as the fluidization agent.¹⁵ The sugar cane straw was ground to about 0.55 mm diameter and fed at rate between 68 and 108 kg/h with air flow of 85 to 95 kg/h. Equivalence ratio was controlled by a combination of adjusting biomass feed and air flow rates. Like the previous work on autothermal pyrolysis, no attempt was made to control pyrolysis temperature, ranging between 470°C and 600°C as equivalence ratio increased from 0.14 to 0.23. Bio-oil yields were remarkably low, dropping from 22.3 wt% to only 9.5 wt% over the range of equivalence ratios tested. High parasitic heat losses can only partly explain these low yields. Biochar yields were very high, reaching 45.8 wt% (30.3 wt% on an ash-free basis) at the lowest equivalence ratio evaluated. The volatile matter content of the biochars was also very high (36.4 wt% for biochar produced at the

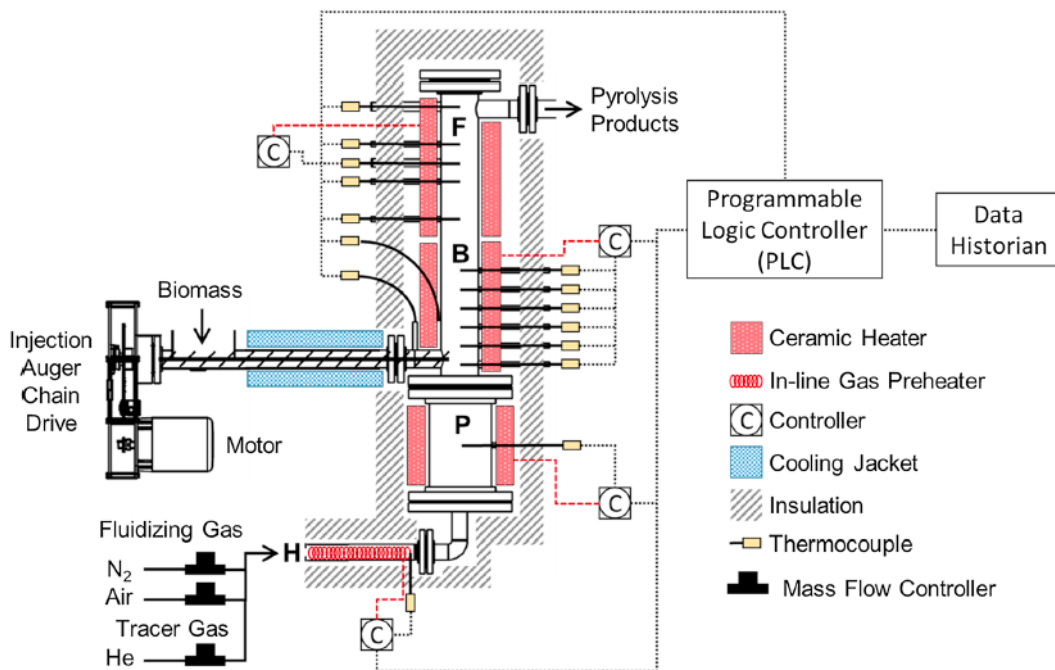
lowest equivalence ratio), suggesting that the reactor was in some respects torrefying rather than pyrolyzing the biomass.

In early 2014, researchers at The University of Western Ontario reported the first study of autothermal pyrolysis in which pyrolysis temperature in a fluidized bed reactor was controlled and the equivalence ratio determined for “energy-neutral” operation.¹⁶ Previous researchers made no attempt to minimize parasitic heat losses from their reactors, which can be notoriously large for small reactors and forces operation at much higher equivalence ratios than otherwise required for autothermal operation. The University of Western Ontario reactor was enclosed in radiant electric heaters that allowed both control of reactor temperature and monitoring of electric power consumption. After determining electric power consumption associated with parasitic heat losses and conventional (that is, nitrogen-blown) pyrolysis of biomass, the air-to-nitrogen ratio of the fluidization gas was increased while holding biomass feed rate and total gas flow rate constant until the enthalpy of pyrolysis was solely provided by partial oxidation. The equivalence ratio for autothermal pyrolysis of birch bark at 500-550°C was found to be 0.050-0.053, in reasonable agreement with values found in Table 1. The authors note that power measurements were “not of very high accuracy” although this uncertainty was not quantified. This might have affected the accuracy of their determinations of equivalence ratio and enthalpy for pyrolysis. Unfortunately, the loss in bio-oil yield (dry basis) as a result of autothermal operation was significant: 22% at 500°C and 31% at 550°C. It is worth noting that the chemical energy lost to the pyrolysis products (bio-oil, biochar, and gas) as a result of autothermal operation was estimated to be 26% at 500°C and 17% at 550°C. This is significantly more than the approximately 8% loss of energy estimated by Equation 1 for autothermal operation. One possible explanation is that the hot filter installed within the freeboard of the reactor might not only have captured char particles but, as a result of

oxidation, heated the char to temperatures that promote cracking of pyrolysis vapors to light gases.¹⁷ In this manner, bio-oil yields might have been substantially reduced even when operating at low equivalence ratios.

We began to explore autothermal pyrolysis at Iowa State University in 2015.¹⁸ Like other researchers working on autothermal pyrolysis, we employed a fluidized bed reactor to exploit its excellent heat and mass transfer characteristics, which prevents the development of hot spots from local imbalances in exothermic and endothermic reactions.¹⁹ Independent of the researchers at The University of Western Ontario, we also realized that the high surface area-to-volume ratio of small reactors would introduce parasitic heat losses to the surroundings that were a large fraction of the energy required to drive pyrolysis reactions. An 8.9 cm diameter fluidized reactor was constructed with multi-point temperature measurements and independently heated plenum, bed, and freeboard using ceramic electric heaters, which allowed control of pyrolysis temperature as equivalence ratio was changed (see Scheme 1).²⁰ Parasitic heat losses from the reactor were determined by fluidizing the bed with nitrogen that was preheated to the set point pyrolysis temperature and measuring the electric power that achieved the set point temperature of the reactor (gray shaded area on the reactor heat power graph of Figure 2). At this point biomass was continuously fed into the base of the fluidized bed, which dropped the reactor temperature until the controller was able to increase electric power to the ceramic heaters and bring the reactor back to the set point temperature. The difference between the new power setting and the power setting required to overcome parasitic heat losses equaled the enthalpy for pyrolysis (red shaded area on the reactor heat power graph of Figure 2). Once steady operation was achieved, air was gradually added to the fluidization gas flow while nitrogen gas flow was reduced to keep volumetric gas flow constant. The resulting exothermic energy release from partial oxidation of the products of pyrolysis caused the power to

the electric heaters to decrease in order to maintain the set point temperature. The equivalence ratio appropriate to autothermal operation of an adiabatic reactor was reached once the electric power fell back to the level of the parasitic heat losses. Thus, it was possible to determine with relatively little effort parasitic heat loss for the reactor, enthalpy for pyrolysis of the biomass feedstock, and equivalence ratio required for autothermal operation of an adiabatic reactor.



Scheme 1. Design of laboratory-scale fluidized bed reactor to simulate adiabatic operation during autothermal pyrolysis investigations. Reproduced from Reference 20. Copyright Applied Energy 2019.

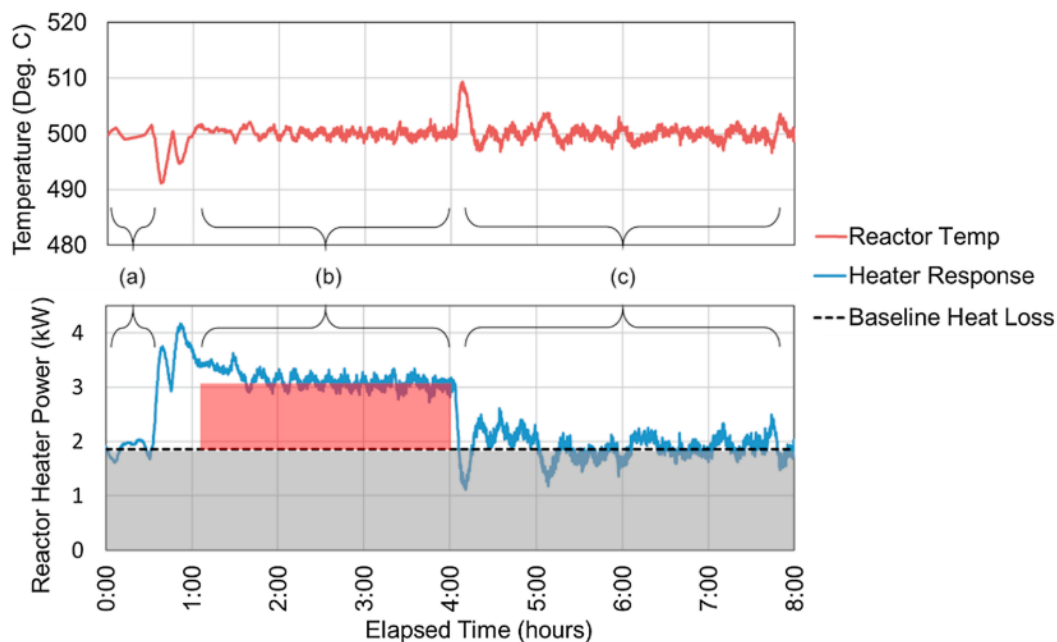


Figure 2. Reactor temperature and heater power during various operational modes of the pyrolyzer: (a) Operation at 500 °C in N₂ without biomass to determine parasitic heat losses (gray shaded area); (b) Operation at 500 °C with biomass to determine enthalpy for conventional pyrolysis (red shaded area); (c) Operation at 500 °C in N₂/air mixture with biomass achieves autothermal pyrolysis (electric power drops back to baseline parasitic heat loss). Reproduced from Reference 20. Copyright 2019 Applied Energy.

We found the enthalpy of pyrolysis for red oak to be 1.14 MJ kg⁻¹ and the equivalence ratio for autothermal pyrolysis to be 0.107.²⁰ A comparison of carbon balances for autothermal and conventional pyrolysis indicates most of the energy for autothermal pyrolysis came from oxidation of light ends and biochar, which had 21.3% and 25% decreases in carbon yields, respectively, compared to conventional pyrolysis (see Figure 3a). The loss of carbon yield for the heavy ends,

the most valuable fraction of bio-oil (consisting of sugars and phenolic compounds) as a result of autothermal operation was only 8%.

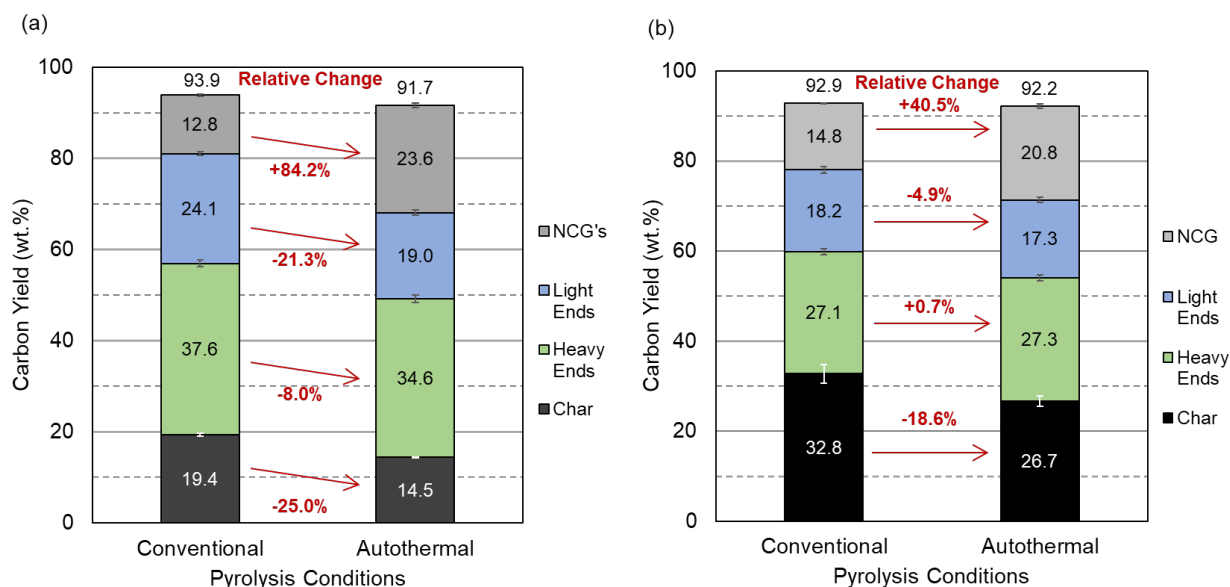


Figure 3. Comparison of carbon yields for conventional pyrolysis and autothermal pyrolysis of (a) red oak and (b) corn stover. Carbon yields (wt%) are calculated on a biomass carbon basis. Reproduced from Reference 20. Copyright 2020 Applied Energy.

In a second paper, we presented results from similar experiments on corn stover.²¹ In this case, the equivalence ratio for autothermal pyrolysis was only 0.068. The reason for this lower equivalence ratio compared to red oak was largely due to differences in char oxidation kinetics, as subsequently discussed. As shown in Figure 3b, this lower oxygen requirement is reflected in smaller losses in carbon yields for light ends (4.9%) and biochar (18.6%). Heavy ends showed a slight increase in carbon yield (0.7%). Although not necessarily statistically significant, it is consistent with the earlier observations of Kim et al.⁵ Taken together, these two papers demonstrate that autothermal operation of fast pyrolyzers for both woody and herbaceous feedstocks can be accomplished at low oxygen equivalence ratios with only modest yield losses for the most valuable pyrolysis products, sugars and phenolic compounds. Just as importantly, these papers

demonstrated for the first time the process intensification that can be achieved by removing the heat transfer bottle neck of conventional pyrolysis, as described below.

Previous studies of autothermal pyrolysis recognized the simplifications that accrue from eliminating combustors, heat exchangers, and piping and conveyance systems associated with moving gaseous or solid heat transfer media in a conventional pyrolysis system. Some of these studies suggested that scale-up to commercial size reactors would be improved through autothermal operation without acknowledging heat transfer as a bottleneck in pyrolysis. In fact, this bottleneck is likely responsible for many failed efforts to commercialize conventional pyrolysis technologies, as a simple analysis demonstrates.

Although chemical kinetics would ideally set the maximum rate that pyrolysis proceeds in a reactor, the transport of heat into the reactor more likely determines this rate. In a recent perspective paper on directly coupled autothermal operation of chemical reactors,²² we showed that the maximum diameter of a tubular reactor to avoid heat transfer becoming the bottle next to processing rates is given by:

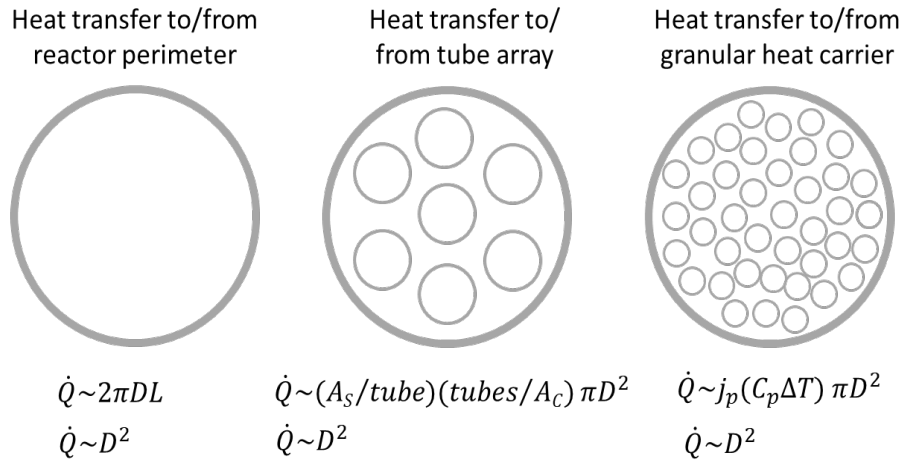
$$D_{max} = 4h\Delta T / (k_{pyr}C_A\Delta H_{r,pyr}) \quad (2)$$

where h ($\text{kJ s}^{-1} \text{m}^{-2} \text{K}^{-1}$) is the heat transfer coefficient, ΔT (K) is the temperature gradient across the wall of the reactor, k_{pyr} (s^{-1}) is the reaction rate coefficient for an assumed first-order pyrolysis reaction, C_A (kg m^{-3}) is the concentration of the reactant, and ΔH_{rx} (kJ kg^{-1}) is the enthalpy change for the pyrolysis reaction. For pyrolysis in a fluidized bed, appropriate values of h and ΔT are $0.1 \text{ kJ s}^{-1} \text{m}^{-2} \text{K}^{-1}$ and 400 K , respectively,²³ k_{pyr} and C_A equal to 0.094 s^{-1} and 180 kg m^{-3} , respectively,²⁴ and $\Delta H_{r,pyr}$ equal to 1000 kJ kg^{-1} .⁷ To avoid heat transfer being a bottleneck to pyrolysis, the tubular pyrolyzer of this example should have diameter no larger than 0.0094 m , which is small even for many benchtop pyrolyzers used in the laboratory. Of course, larger reactors are designed

to enhance the surface area-to-volume ratio of the heat exchangers employed, but the constraint is generalized for any kind of heat transfer process, as shown in Scheme 2. It should be noted that although the conveyance of hot granular materials into fluidized beds or auger reactors represents direct contact heat transfer with very high surface area-to-volume ratio, it is the rate of conveyance of granular materials into the reactor rather than intraparticle or interparticle heat transfer that is typically rate limiting in this case.

This analysis further suggests that substituting an exothermic chemical reaction for heat transfer to provide the enthalpy for pyrolysis should allow significant process intensification, defined here as the ratio of biomass throughput under autothermal operation to the throughput under nitrogen-blown operation in the same sized reactor. We attempted process intensification once autothermal operation was established for the nominal biomass feed rate of conventional pyrolysis by increasing the amount of oxygen beyond that required for autothermal operation, which allowed us to increase the feed rate of biomass. In practice, this was accomplished at constant oxygen equivalence ratio appropriate for autothermal operation and constant volumetric gas flow appropriate to fluidizing the 8.9 cm diameter reactor by increasing the percent of air in the air/nitrogen mixture used to fluidize the reactor. The maximum feed rate of red oak into a nitrogen-blown (115 L min^{-1}) fluidized bed pyrolyzer operated at 500°C was only 4.78 kg/h. This throughput was achieved autothermally by replacing the nitrogen gas flow with a mixture of 31 vol% air and 69 vol% nitrogen at constant gas flow rate, which represents an oxygen concentration of 6.5% and an equivalence ratio of 0.1073. Although this condition does not provide process intensification, by further increasing the percent of air in the mixture, the feed rate of red oak can be increased while maintaining both the oxygen equivalence ratio and the pyrolysis temperature. In this manner, the feed rate of red oak was increased to 15.4 kg/h, representing process

intensification of 3.2, beyond which no further intensification was possible in these particular experiments as the fluidization gas was 100% air (21% oxygen).²⁰ In a similar manner, air-blown autothermal pyrolysis of corn stover achieved process intensification of 2.8.²¹ Further intensification would require schemes that increase the delivery of oxygen to the reactor such as using pressurized air or oxygen-enriched air or employing reactor designs capable of accommodating higher volumetric gas flow rates.



Scheme 2. Heat transfer \dot{Q} into a cylindrical pyrolyzer of fixed diameter-to-length ratio is proportional to the square of reactor diameter D regardless of how heat is delivered (L : reactor length; $A_s/tube$: surface area of a heat transfer tube in the reactor; $tubes/A_c$: number of tubes per cross-sectional area of the reactor; j_p : mass flux of granular heat carrier entering the reactor; $C_p \Delta T$: sensible energy per unit mass of granular heat carrier). Reproduced from Reference 22. Copyright 2020 Joule.

The advantage of autothermal operation increases as a pyrolyzer is scaled in size, as illustrated in Figure 4. If heat transfer is rate limiting for pyrolysis, throughput will scale as the square of reactor diameter. In contrast, if the energy for pyrolysis is provided by an oxidation reaction, throughput will scale as the cube of reactor diameter.²² As a result, the intensification achieved from autothermal operation of a pyrolyzer is expected to scale linearly with the diameter of the reactor as long as limitations do not arise on the rate that oxidation reactants can be supplied to the reactor. For example, a fluidized bed reactor in which the ratio of superficial gas velocity to

minimum fluidization velocity and particle size distribution of fluidization media are held constant would have more constrained intensification than predicted by Figure 4.

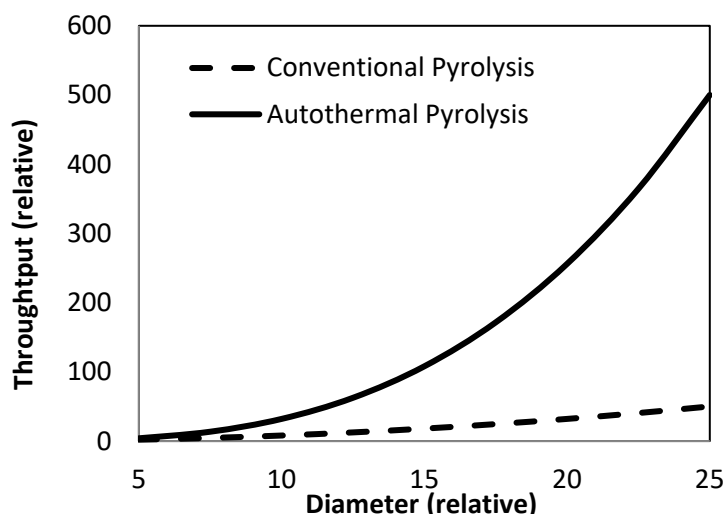


Figure 4. Throughput for a conventional pyrolyzer limited by heat transfer scales as the square of reactor diameter while an autothermal reactor with throughput limited by chemical kinetics scales as the cube of reactor diameter. Process intensification from autothermal operation scales linearly with reactor diameter. Reproduced from 22. Copyright 2020 Joule.

This difference in scaling yields economic advantages for autothermal pyrolysis beyond eliminating costs for ancillary heat transfer equipment. Capital cost for a heat transfer limited pyrolyzer increases linearly with reactor throughput and no economies of scale are captured in making the reactor larger. In contrast, capital costs for a chemical kinetic limited pyrolyzer increases as the two-thirds power of throughput, following the classical economy-of-scale principle.²⁵ As illustrated in Figure 5, the relative cost of reactors for conventional and autothermal pyrolysis are expected to increasingly diverge as reactor throughput increases.

In view of the complexities of the chemical kinetics of partial oxidation of pyrolysis products, some fortuity must be assigned to successful operation of autothermal pyrolyzers. Whereas the products of autothermal gasifiers and steam reformers approach chemical equilibrium distributions, autothermal fast pyrolysis is inherently involves non-equilibrium reactions, as

evidenced by the products of this relatively high temperature process being predominantly liquid. Predicting the product distribution of an equilibrium process is simply a matter of knowing the Gibbs free energies for potential products while achieving the equilibrium distribution of products in practice is a matter of assuring good heat and mass transfer and providing sufficient residence time for reaction.

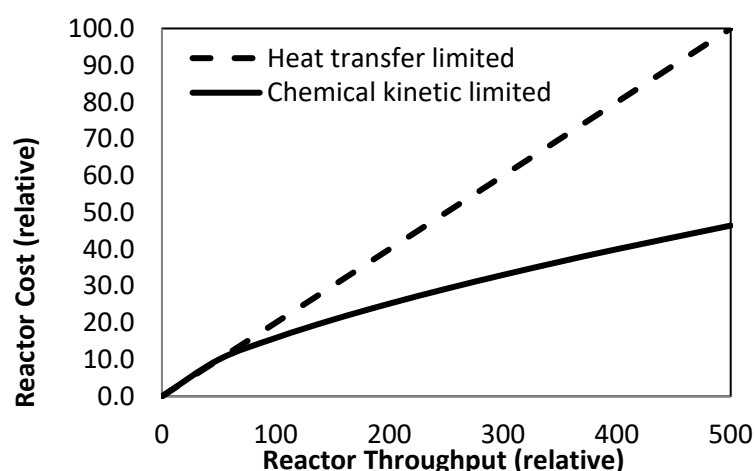


Figure 5. Cost scales linearly with throughput for a conventional pyrolyzer while and autothermal pyrolyzer scales as the $2/3$ power of reactor throughput. Reproduced from Reference 22. Copyright 2020 Joule.

In contrast, predicting product distribution in a non-equilibrium process requires detailed kinetic data on major reactants and intermediate products as well as models of the hydrodynamics of the reactor.^{26,27} Progress has been hampered by the difficulty in interrogating the condensed phase reactions responsible for depolymerization of carbohydrate²⁸ and lignin²⁹ in biomass. Accounting for reactions responsible for the prominent intermediate and final pyrolysis products, which includes light (permanent) gases like carbon monoxide and low molecular weight hydrocarbons, light (condensable) oxygenates such as alcohols, aldehydes and carboxylic acids, and heavy organics consisting mostly of saccharides and phenolic compounds,³⁰ is also daunting. Furthermore, efforts are just emerging to include partial oxidation of pyrolysis products in

computational models for the purpose of simulating autothermal pyrolysis.^{31–33} Efforts to date to include elementary oxidation reactions in pyrolysis reaction mechanisms are more appropriate for high temperature ($>1000^{\circ}\text{C}$) processes that proceed to the equilibrium products of carbon dioxide and water.³⁴ These do not appear to correctly predict rates at the lower temperatures typical of fast pyrolysis ($400\text{--}600^{\circ}\text{C}$).³⁵

The identity of pyrolysis products being oxidized during autothermal pyrolysis can be deduced from the autoignition temperatures of representative light gases, light oxygenates, heavy organics and solids produced during pyrolysis, some of which are shown in Table 2. These values should be considered approximate as autoignition temperatures are notoriously difficult to measure, depending heavily on the design and operation of the apparatus used to measure them.³⁶ Nevertheless, the table indicates that permanent gases and phenolic compounds are unlikely to be oxidized at 500°C while light oxygenates and char have autoignition temperatures favorable for reaction at pyrolysis temperatures, which is consistent with the yield changes observed for autothermal pyrolysis (Figure 3). By design, the residence times of vapors and gases in fluidized bed pyrolyzers are as much as a thousand times shorter than for biochar, with the result that oxidation of biochar provides the largest contribution toward the enthalpy for pyrolysis. Measurements of steady-state char loading in a fluidized bed operated as a conventional pyrolyzer²¹ indicate residence times between 15–30 minutes compared to only a few seconds for gases and vapors, explaining biochar’s role as a major source of energy for autothermal pyrolysis products.^{37–39}

Table 2. Approximate autoignition temperature for different categories of pyrolysis

Category	Compound	Approximate autoignition temperature (°C)
Permanent gases	Hydrogen	500
	Methane	560
	Carbon monoxide	610
	Ethane	515
Light oxygenate vapors	Formaldehyde	424
	Acetaldehyde	150
	Propanal	207
	Acetic acid	460
	Furfural	316
Heavy organic vapors	Phenol	650
Solids	Charcoal	350

We have recently investigated oxidation rates of char produced from several kinds of biomass at temperatures much lower than previously considered in char combustion studies.⁴⁰ Experiments were performed in a 3.8 cm dia. fluidized bed and data was analyzed assuming first order kinetics relative to carbon consumed. At the lowest reaction temperatures (less than about 500°C), for which biochar oxidation is under chemical kinetic control, reaction rate constants were strongly dependent on the type of biomass from which the biochar was derived (see Figure 6). This dependence correlated with ash content of the biochar. In particular, activation energy for biochar oxidation decreased from around 130 kJ mol⁻¹ to around 110 kJ mol⁻¹ mol as potassium content increased from 0.3 wt% to 2.25 wt% in the biochar. This catalytically effect was reduced 50% to

85% by washing the biochar with dilute mineral acid to remove ash,⁴⁰ which is important to subsequent discussions of the use of biomass pretreatments to enhance pyrolytic sugar production.

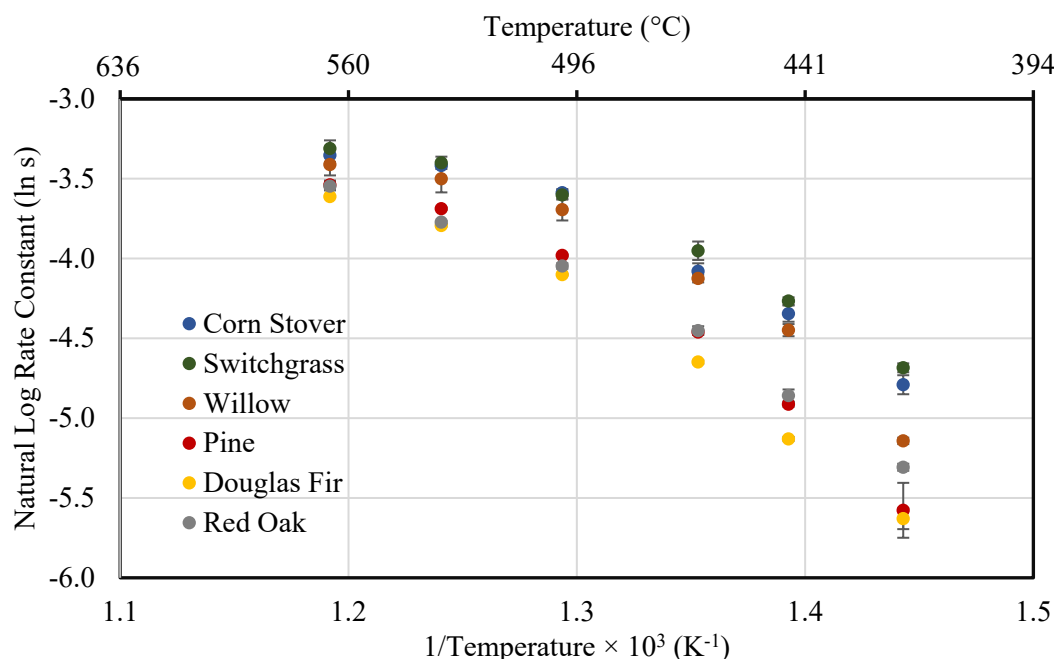


Figure 6. Biochar oxidation rate constants were strongly dependent on the type of biomass from which the biochar was obtained as reaction temperature decreased and oxidation came under chemical kinetic control (less than about 500°C). Reproduced from Reference 40. Copyright 2020 Chemical Engineering Journal.

The catalytic effect of ash on biochar oxidation is important in understanding why autothermal pyrolysis of corn stover was sustained at an equivalence ratio of only 0.068 while red oak required a much higher equivalence ratio of 0.107 despite having significantly lower heating value and similar enthalpy for pyrolysis as red oak (see Table 1). Whereas non-catalyzed reaction of solid carbon in biochar with molecular oxygen usually produces CO, alkali and alkaline earth metals in the char adsorb oxygen and participate in a catalytic reduction/oxidation cycle directly producing CO₂.⁴¹ Because the enthalpy of reaction for conversion of solid carbon into CO₂ is 2.5 times higher than conversion to CO, it is expected to consume less char and oxygen to provide the energy for pyrolysis. As shown in Figure 7, the molar ratio of CO to total carbon oxides (CO + CO₂) increased linearly with potassium content of the biochar. Specifically, at 500°C this ratio increased from

0.71 for red oak to 0.86 for corn stover; that is, the relative amount of CO₂ to CO was 2.5 times higher in the products of corn stover oxidation than in the products of red oak oxidation. Accordingly, high ash content biomass is expected to have several advantages over lower ash content biomass in autothermal pyrolysis: oxygen demand (equivalence ratio) is reduced; higher feed rates of biomass can be employed in a reactor of given dimensions; and less biochar is oxidized. All of these phenomena were observed in our pilot-scale experiments in autothermal pyrolysis.^{20,21}

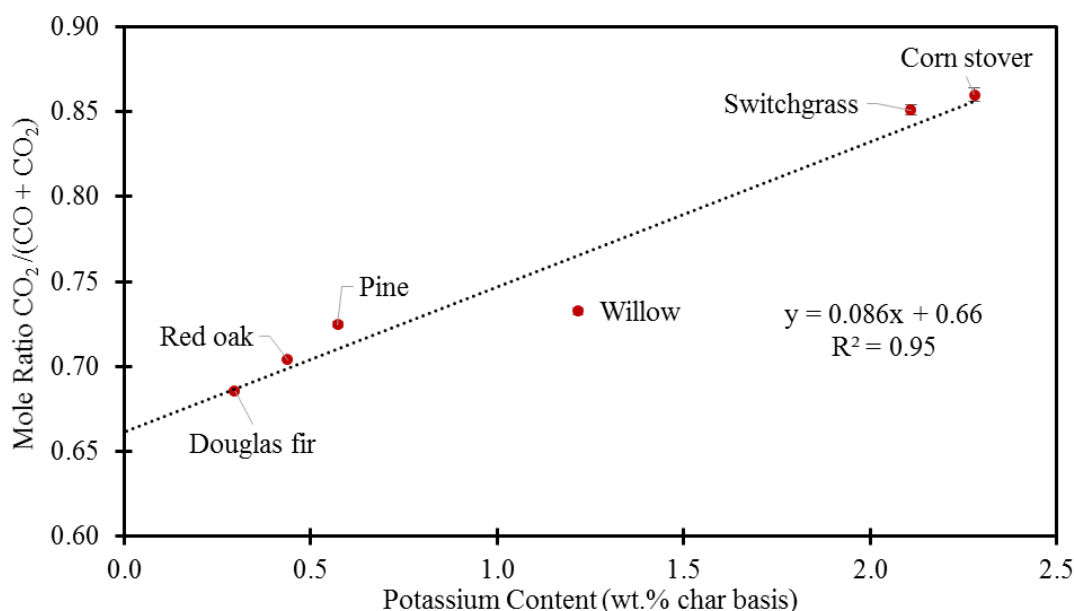


Figure 7. The potassium in high ash biomass catalyzes more complete oxidation of biochar to carbon dioxide, reducing equivalence ratio, increasing biomass throughput, and reducing char consumption in autothermal pyrolysis. Reproduced from Reference 40. Copyright 2020 Chemical Engineering Journal.

In an effort to better understand whether organic vapors produced during pyrolysis were significantly oxidized during autothermal pyrolysis, we fractionated the heavy ends of bio-oil using two stages of liquid-liquid extraction.²⁰ Liquid extraction with water separated the heavy ends into water-insoluble phenolic compounds and water-soluble pyrolytic sugars. Liquid extraction with toluene separated the water-insoluble fraction into mostly phenolic monomers

(soluble in toluene) and phenolic oligomers (insoluble in toluene). Comparing the yields of these three fractions for conventional and autothermal pyrolysis of red oak showed oxidative conditions reduced pyrolytic sugars by 19.7% and phenolic monomers by 40.5% while phenolic oligomers, the largest fraction of heavy ends, showed no statistically significant change.

The nature of the oxidation of phenolic oligomers was investigated by subjecting the toluene insoluble phenolic compounds to NMR analysis.⁴² ³¹P NMR revealed decreases in phenolic hydroxyl groups (C5-substituted, guaiacyl phenolic, catechol type, and P-hydroxyl-phenyl). We observed no increase in carboxylic acid functionality for phenolic monomers produced under autothermal pyrolysis while ¹³C NMR revealed a large increase in aromatic carbonyls (see Table 3). Taken together, these results indicate autothermal pyrolysis promoted oxidation of phenolic monomers to aldehydes and ketones. Future studies are planned to investigate the oxidation of saccharides produced during pyrolysis.

Table 3. Autothermal pyrolysis encourages addition carbonyl functionality on phenolic compounds released from lignin.

Functional Group	δ (ppm)	% of Carbon Bonds	
		Non-Oxidative	Oxidative
Carbonyl	215.0-166.5	2.68	3.06
Aromatic C-O Bond	166.5-142.0	17.30	19.25
Aromatic C-C	142.0-125.0	39.49	36.20
Aromatic C-H	125.0-95.8	13.18	14.05
Aliphatic C-O	95.8-60.8	2.90	2.89
Methoxly-Aromatic	60.8-55.2	15.43	16.37
Aliphatic C-C	55.2-0.0	9.02	8.18

ENHANCING PYROLYTIC SUGAR PRODUCTION

Even before Steven Chu became Secretary of Energy in the Obama administration, he conceived of a “glucose economy” to supplant petroleum as the world’s major source of energy.⁴³ He proposed cultivation of fast-growing lignocellulosic biomass in the tropics and the conversion of the cellulose in the harvested biomass into glucose. This sugar would be shipped around the

world as a commodity chemical for production of fuels and chemicals. This scenario assumed that cellulose would be depolymerized via enzymatic hydrolysis to glucose, much as starch is hydrolyzed to dextrose, and was the original basis for much of the biofuels research at the Bioenergy Research Centers established by the U.S. Department of Energy (DOE) in 2007.⁴⁴ Despite advances in deconstructing lignocellulosic biomass, identifying enzyme cocktails to efficiently hydrolyze polysaccharides and genetically modifying microorganisms to ferment less than pristine substrates,^{45,46} commercialization of biofuels from cellulosic sugars has remained elusive.⁴⁷ Among the major challenges has been the high cost of pretreatments to separate polysaccharides from lignin, production of cost-effective enzyme cocktails, and effective use or disposal of process wastes.⁴⁶

We propose thermal depolymerization of biomass, using heat instead of enzymes to break glycosidic bonds in plant polysaccharides, as an alternative pathway to cellulosic sugars.²⁸ This pathway has been less explored than acid and enzymatic hydrolysis, likely because the low selectivity and unfavorable thermodynamics of high temperature thermal processes would suggest poor prospects for thermal depolymerization. Indeed, pyrolysis of most lignocellulosic biomass yields very little sugar (see Figure 8), with yields that at best are only a few percent of the theoretical yields of hexose and pentose from cellulose and hemicellulose. The reason for these poor sugar yields is hinted at in Figure 8, where sugar yields from red oak are almost four times higher than from corn stover despite having only 23% more polysaccharides (cellulose and hemicellulose) than corn stover.⁴⁸ The important compositional difference between these two feedstocks is the amount of ash, specifically alkali and alkaline earth metals (AAEM), which occur at much higher concentrations in corn stover. The AAEM content, which includes potassium, sodium, calcium, and magnesium, for corn stover and red oak is 1.17% and 0.17%, respectively,

with potassium being the largest contributor to AEEM in corn stover while calcium plays that role in red oak.⁴⁸

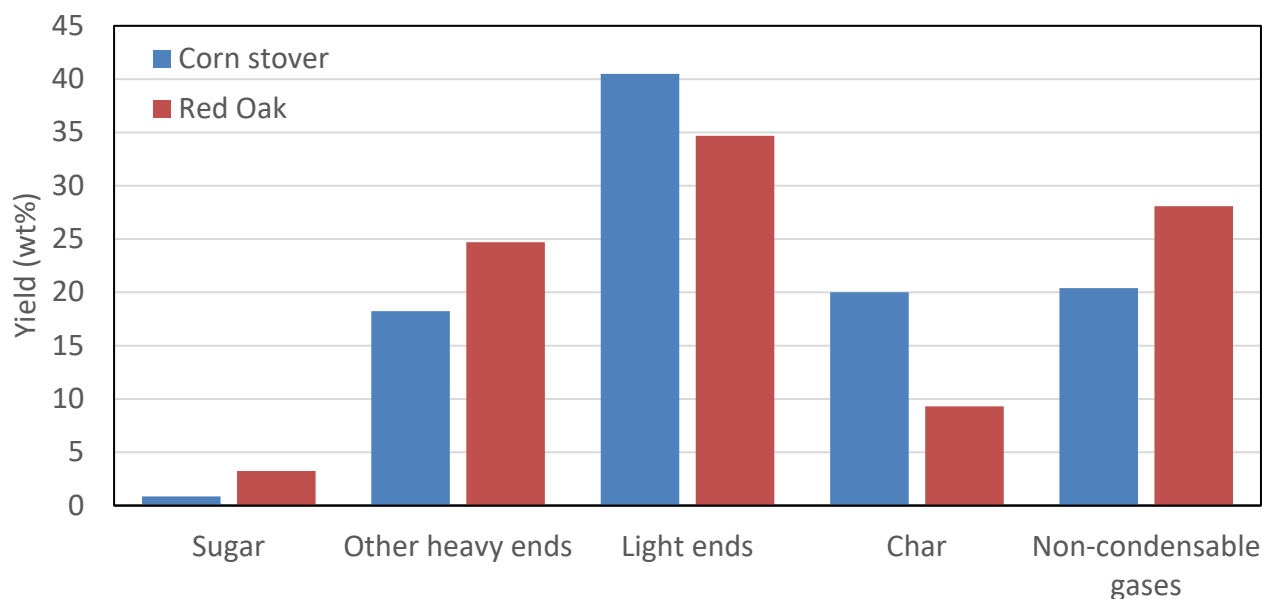


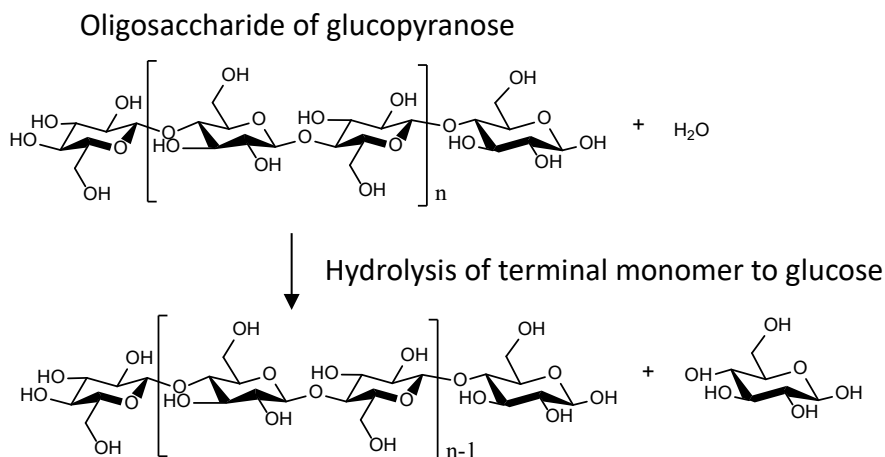
Figure 8. Sugar yield from pyrolysis of untreated biomass is very low compared to other pyrolysis products. The effect is particularly prominent for high ash feedstocks (like corn stover) compared to low ash feedstocks (like red oak). Yields of light ends and char also correlate to ash content. Similar results are observed for conventional pyrolysis of untreated biomass. Based on unpublished data from autothermal pyrolysis of untreated biomass at Iowa State University.

In the absence of AAEM, the yields of sugars from thermal depolymerization of saccharides can be significant although the products are often anhydrosugars instead of fully hydrated carbohydrates.⁴⁹ For example, whereas hydrolysis of oligosaccharides of glucopyranose yields glucose as a result of the participation of water in the reaction, thermal depolymerization is a “dry decomposition” reaction producing dehydrated (anhydro) sugars instead, as illustrated in Scheme 3a. Interestingly, the yield of levoglucosan from pyrolysis of glucopyranose increases in going from monomers to dimers and oligomers (structural representations of these saccharides are provided in Scheme 4) with cellulose approaching 60 wt% yield (Table 4).⁵⁰

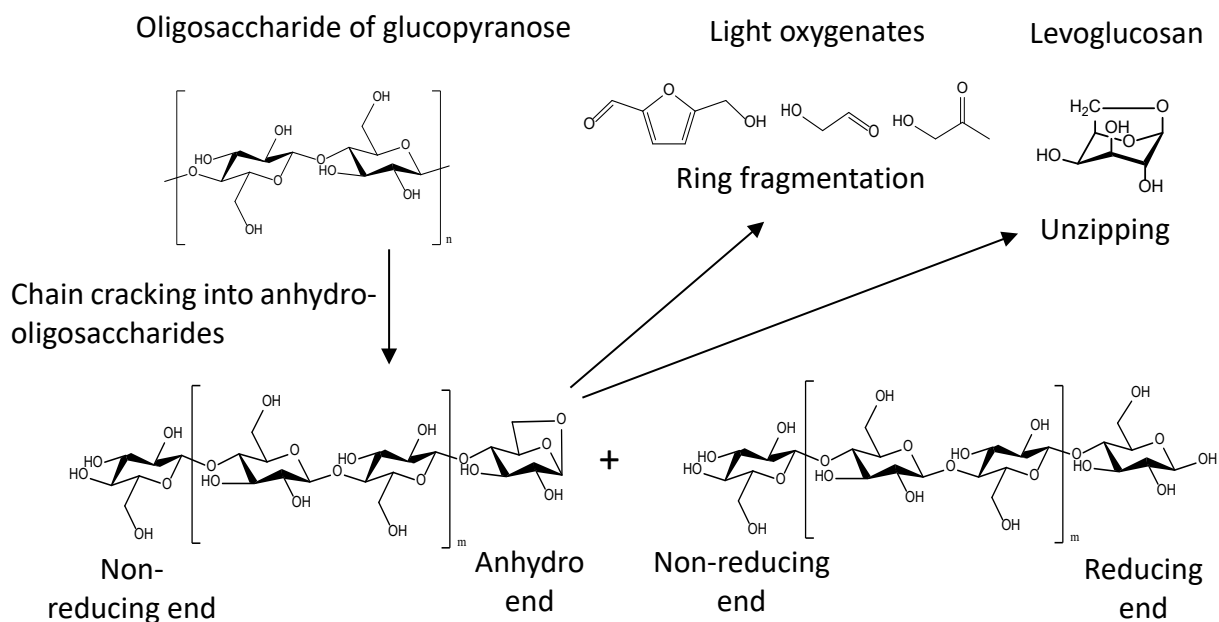
The fact that pyrolysis of cellulose produces levoglucosan instead of glucose is fortuitous for advancing the prospects for “pyrolytic sugar production.” Glucose has a vapor pressure one

thousand-fold lower than for levoglucosan.⁵¹ Glucose would not be able to escape the hot environs of a pyrolyzer once formed, resulting in its decomposition to more volatile products. On the other hand, the vapor pressure of levoglucosan at pyrolysis temperatures is high enough to allow it to volatilize and escape with other products of pyrolysis.¹

(a)

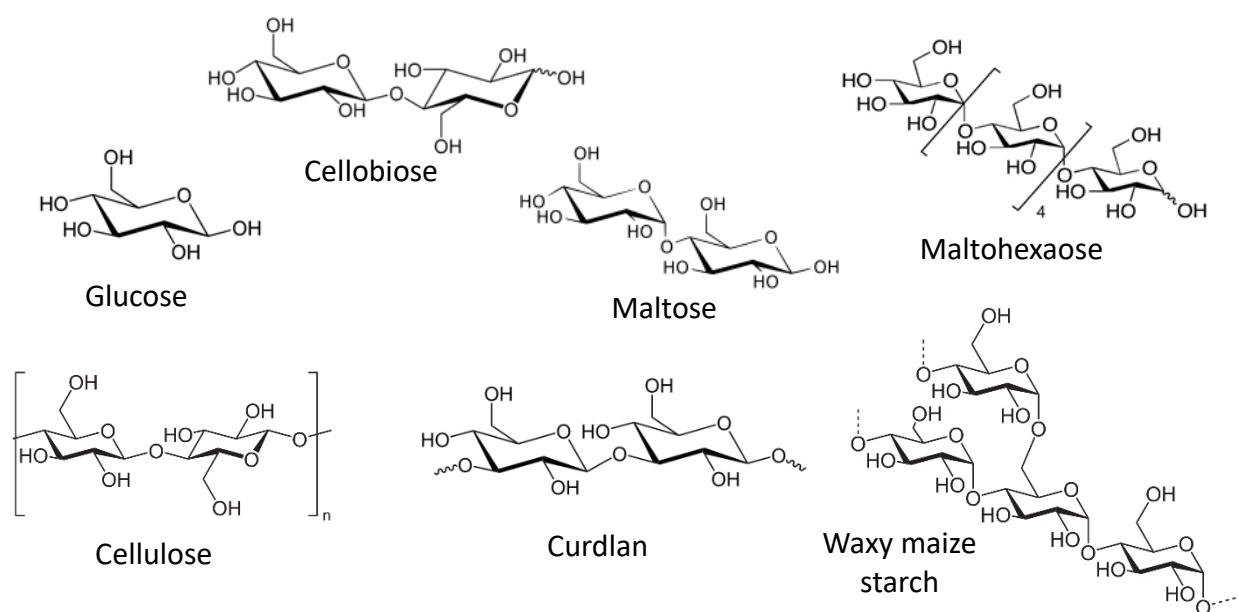


(b)



Scheme 3. Depolymerization of oligosaccharide. (a) Enzymatic or acid hydrolysis to glucose; (b) thermal depolymerization of oligosaccharide of glucopyranose (unzipping can occur at either an anhydro or non-reducing terminal unit on the chain while chain cracking and ring fragmentation can occur anywhere along the chain).

The reason for yields being less than 100 wt% even for pure pyranose samples is illustrated in Scheme 3b. Thermal depolymerization begins by cracking an oligosaccharide into two smaller chains, one of which contains a double ring structure at the end of the chain where normally a reducing end arising from hydrolysis would be found. Mid-chain and end-chain fragmentation of pyranose rings can also occur, producing low molecular weight, oxygenated compounds. Breaking of glycosidic bonds that attach either anhydro or non-reducing terminal units to the chain, known as unzipping reactions, produce levoglucosan.⁵² The competition between unzipping and fragmentation reactions also explains why the “light ends” of bio-oil increases when sugar decreases.⁵³



Scheme 4. Structures of several glucopyranose monomers, oligomers, and polymers for which yields of levoglucosan are reported in Table 4.

Alkali and alkaline earth metals are powerful catalysts for fragmenting glucopyranose rings, as illustrated in Figure 9.⁵⁴ Addition of as little as 0.01 mmoles of AAEM salts per gram of glucopyranose can reduce levoglucosan yields by between 40% (alkaline earth metals) and 66% (alkaline metals). This decrease correlates as well with the increase in production of smaller oxygenated molecules like formic acid, acetol and furfural, among others, shown in Figure 9.

Table 4. Yields of levoglucosan from various glucopyranose monomers, oligomers, and polymers.⁵⁰

Compound	Glucose (wt%)	Maltose (wt%)	Cellobiose (wt%)	Malto-hexaose (wt%)	Curdlan (wt%)	Waxy maize starch (wt%)	Cellulose (wt%)
Levoglucosan	7.00	20.5	24.4	33.1	44.2	48.5	58.8

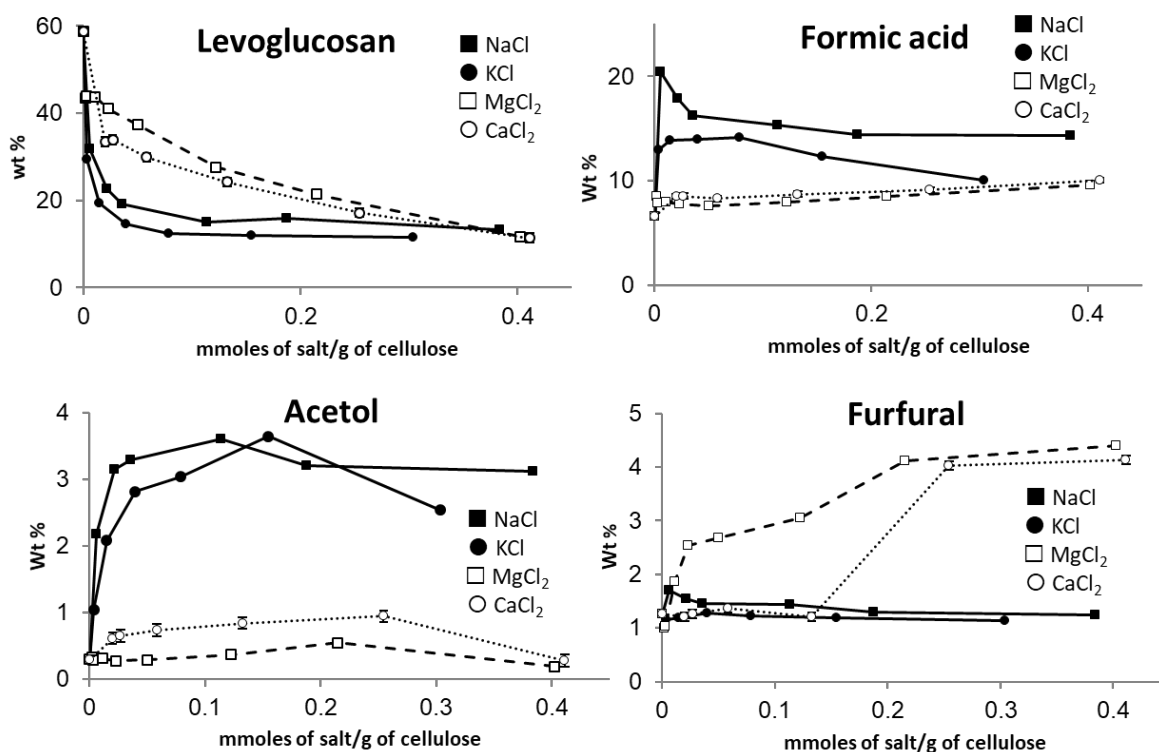


Figure 9. Effect of alkali and alkaline earth metals on products of cellulose pyrolysis. Reproduced from Reference.⁵⁵ Copyright 2010 Bioresource Technology.

The thermal depolymerization of hemicellulose is less well understood. The pyrolysis of pure hemicellulose might be expected to yield anhydrosugars from the monomeric units of hemicellulose: glucopyranose, xylopyranose, mannopyranose and galactopyranose. However, the extraction of hemicellulose or xylan from biomass is usually achieved via alkaline treatments, resulting in samples being heavily contaminated by AAEM, complicating the conduct of experiments with pure samples of these polysaccharides. Patwarden et al.⁵⁶ employed dialysis to

reduce ash content to less than 0.1 wt% in extracted hemicellulose and 0.9 wt% in commercial xylan, which are an order of magnitude lower than found in the original samples. Indeed, pyrolysis of these substantially de-ashed samples yielded dianhydro xylose and anhydro xylopyranose. However, in sum these anhydrosugars represented only 12.6 wt% of the products, much lower than achieved from pyrolysis of pure cellulose, with light oxygenates and gases produced in much greater quantities. If AAEM are as potent ring fragmentation catalysts for hemicellulose as for cellulose, this low yield of anhydrosugars is not surprising as the AAEM remaining in the hemicellulose samples even after dialysis was twice the concentration responsible for reducing the yield of levoglucosan from cellulose to less than 20 wt%.

Interestingly, pyrolysis of demineralized hemicellulose produced xylose at yields approaching 5 wt%. Since xylose from hemicellulose or xylan is thought to be the product of hydrolysis, Patwardhan et al.⁵⁶ hypothesized that produced water, which represented about 15 wt% of products, was in sufficient quantity to drive hydrolysis. Interestingly, the vapor pressure of xylose is only about ten times lower than for levoglucosan, suggesting it might be sufficiently volatile to escape the pyrolysis reactor, unlike glucose. Although these experiments, conducted in a micropyrolyzer, found no mannose or galactose among the products of hemicellulose or xylan pyrolysis, more recent studies in our laboratory with as-received red oak in a fluidized bed pyrolyzer found significant quantities of these two monosaccharides as well as xylose, each produced at about 20% of the yield of levoglucosan, the dominant sugar product.⁵⁷ On the other hand, no anhydrosugars of xylose were detected among the products.

As early as 1924, Venn⁵⁸ reported that pretreatments of raw cotton prior to thermal decomposition could dramatically increase the yield of levoglucosan from these cellulose-rich fibers. Pretreatments included repeated washing in distilled water, soaking in dilute hydrochloric

acid, boiling in dilute acid or caustic soda solution, and various combinations of these pretreatments. Slow pyrolysis at 355°C for 40 minutes increased levoglucosan yields from essentially zero for raw cotton to as high as 36% for one of the pretreatments involving acidification. Although Venn noted that effective pretreatments reduced the ash content of cotton samples, he speculated that improvements in levoglucosan yields were due to acid-promoted depolymerization or intermolecular rearrangements of the cellulose.

For the next fifty years thermal depolymerization of biomass was little studied with most research on production of cellulosic sugars focused on acid or enzymatic hydrolysis of polysaccharides. Fast pyrolysis of biomass in continuous reactors was not even developed until the 1970's.⁵⁹ Even then, the goal was to convert biomass into a liquid fuel of high volumetric energy density suitable for direct firing in boilers or upgrading into hydrocarbon transportation fuels.³⁰ A prominent exception was the work of Shafizadeh et al.⁶⁰ in 1979, who proposed acid washing/prehydrolysis of cellulosic feedstocks for the industrial production of levoglucosan via pyrolysis. In small-scale (5 g) experiments acid pretreatment of various cotton products (Whatman filters, linters and fabric) produced levoglucosan yields approaching that from pure microcrystalline cellulose. However, they were unable to definitively conclude whether their results were attributable to “removal of inorganic impurities, addition of trace amounts of acid, or changes in the crystallinity or fine structure of the cellulose.”

Ten years later Scott and co-workers⁶¹ at the University of Waterloo, Canada revived the goal of producing pyrolytic sugars. They definitively attributed enhanced sugar yields from poplar wood to the removal of alkaline cations from the biomass by acid washing although they were uncertain whether cations were retarding the unzipping of levoglucosan from the terminal units of

cellulose or catalyzing pyranose ring fragmentation. The exact mechanism by which AAEM acts on polysaccharides is still debated.^{62–64}

A little more than twenty years after the original pyrolytic sugar studies of Shafizadeh et al.⁶⁰ and in collaboration with some of Scott's earlier collaborators, we explored water and acid leaching and acid hydrolysis of herbaceous biomass, which has higher AAEM content than the cellulose products and woody biomass of earlier studies.⁶⁵ While water leaching was ineffective, the two acid-based pretreatments enhanced sugar yields at levels similar to what had been achieved with lower ash (woody) feedstocks of previous studies.

Demineralization of thermochemical processing feedstocks through leaching with water or dilute acid solutions has been pursued for several reasons including reducing ash fouling during combustion and gasification, improving the yield and quality of pyrolysis liquids (bio-oil), and mitigating catalyst poisoning in subsequent upgrading of products of pyrolysis and gasification.⁶⁶ Although inexpensive mineral acids such as sulfuric acid are frequently employed in leaching studies, carboxylic acids have also proved effective.⁶⁷ Oudenhoven et al.⁶⁸ suggested the use of an acetic acid-rich aqueous phase selectively condensed from bio-oil vapors as an inexpensive leaching medium.

As early as 1999, our research group compared fast pyrolysis to acid hydrolysis and enzymatic hydrolysis for production of cellulosic ethanol from woody biomass.⁶⁹ The pyrolysis approach was based on the work of Scott et al.⁶¹ ten years earlier. This study found that while enzymatic hydrolysis achieved the lowest selling price for ethanol, fast pyrolysis came within 23% of this price, which is within the uncertainty of technoeconomic analysis (30%). A more comprehensive and recent study by Oudenhoven⁷⁰ draws a less optimistic conclusion. Leaching and drying the biomass and treating the wastewater from leaching adds 35% to the capital cost of the pyrolysis

plant. The large volumes of process water required to thoroughly remove AAEM from biomass and the subsequent burden of wastewater treatment were largely responsible for increasing operating costs by as much as 50%. The gain in earnings from sugar and phenolic oil products was insufficient to make the process profitable for either wood or straw feedstocks (although use of low-cost bagasse achieved marginal profitability).

The challenge with biomass leaching for production of pyrolytic sugars is the need to reduce concentration of AAEM below 0.05% to overcome these powerful ring fragmentation catalysts. Accordingly, we have been exploring passivation rather than removal of AAEM from biomass. In this approach, a reagent is added to the biomass to convert AAEM into thermally stable compounds unreactive toward ring fragmentation of polysaccharides. Considering the relatively low concentration of AAEM in biomass, an equimolar passivation reaction would require very little reagent. To facilitate application of a passivation reagent into biomass, it should be water soluble, allowing dilute solutions to be sprayed on the biomass, thoroughly wetting particle surfaces and facilitating diffusion of the reagent into the interior of the particles. Although the reagent infused biomass requires drying before pyrolysis, no wastewater is generated, unlike acid leaching of AAEM.

We have found some of the same mineral acids used to leach AAEM from biomass are also effective as passivation agents.⁴⁸ We hypothesize that AAEM normally chelated into the polymeric structure of biomass⁷¹ reacts with the acid to form salts in which the large anions shield the smaller AAEM cations from interacting with the biomass. For example, sulfuric acid (H_2SO_4) reacts with potassium to form potassium sulfate (K_2SO_4) and potassium hydrogen sulfate (KHSO_4), the former of which decomposes above 1689°C (its boiling point) and the latter decomposes above 300°C to potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$) that in turn decomposes to K_2SO_4 above 600°C. Thus, sulfuric

acid converts AAEM into salts stable against thermal decomposition at pyrolysis temperatures (400-600°C).

An example of the dramatic impact of AAEM passivation on products of pyrolysis is illustrated in Figure 10. We infused switchgrass samples with various mineral and carboxylic acids equal to 2 wt% of the biomass sample.⁴⁸ Infusion involved dissolving 0.1 g of acid in 15 g of water and mixing the solution with 5 g of biomass. The damp biomass was not washed after this treatment, making this process distinct from typical leaching pretreatments, but dried before pyrolysis in a microreactor at 500°C. Sulfuric acid and phosphoric acid (H₂PO₄) infusions increased anhydrosugar yields from switchgrass around six-fold compared to untreated switchgrass. Furanic products approximately doubled, suggesting that the acid encouraged dehydration of carbohydrate. Light oxygenates dropped by 65% as would be expected if the relative rates of unzipping and ring fragmentation illustrated in Scheme 3b shifted in favor of the former reaction. Hydrochloric acid (HCl) produced about half the anhydrosugar yields as H₂SO₄ and H₂PO₄, possibly reflecting the

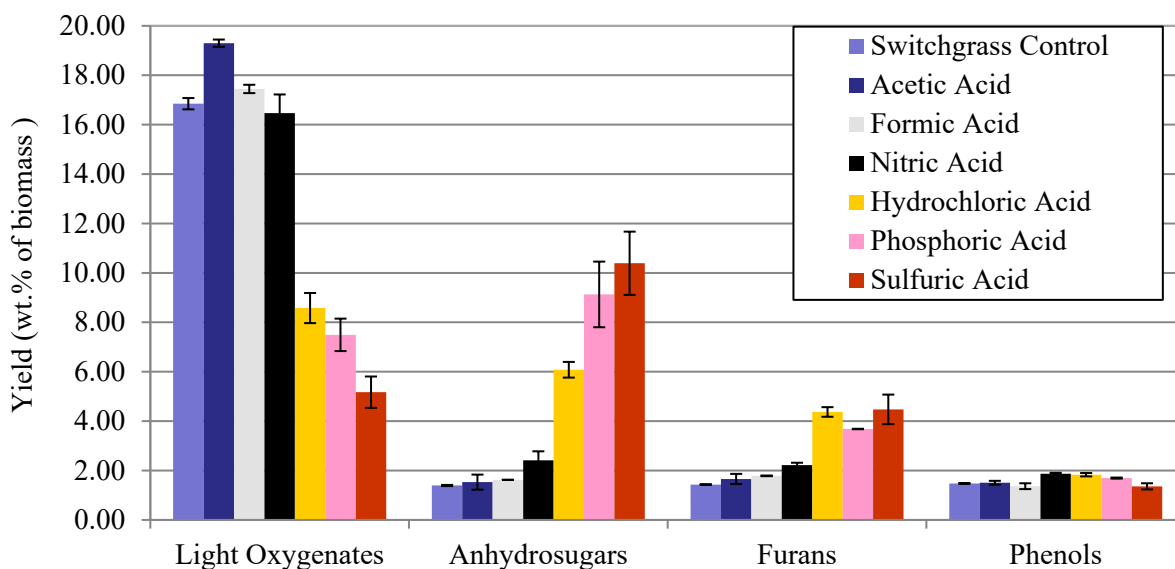


Figure 10. Yield of volatile compounds for pyrolysis of switchgrass at 500°C after pretreatment with infusions of various acids equal to 2 wt% of the biomass. Reproduced from Reference 48. Copyright 2012 ChemSusChem.

smaller shielding effect of the chloride ion. Nitric acid (HNO_3) and the two carboxylic acids (acetic and formic) produced no statistically significant difference in yields compared to the control case. We think this reflects decomposition temperatures for the corresponding AAEM salts that are generally below pyrolysis temperatures, reactivating AAEM as pyranose ring fragmentation catalysts during pyrolysis.

In these micropyrolysis experiments, levoglucosan was the major anhydrosugar product.⁴⁸ Yields of levoglucosan on a cellulose basis from sulfuric acid pretreated biomass were as high as 59%, essentially equal to the yield from pyrolysis of pure nanocrystalline cellulose. We discovered that there was an optimal level of acid pretreatment, with levoglucosan yields falling off on either side of this optimal (over pretreatment appeared to promote dehydration to furanic products). As illustrated in Figure 11, the optimal molar addition of acid correlated closely to the moles of AAEM in the biomass. This correlation was improved by subtracting out the moles of chlorine found in the biomass from the AAEM content, reflecting the fact that AAEM existing as chloride was already a thermally stable salt.⁴⁸ A follow on study demonstrated that levoglucosan yields for several biomass feedstocks were almost independent of temperature in the range of 350 to 500°C.⁷²

The practical implementation of pyrolytic sugar production requires scaling from hundred microgram batch experiments of the original AAEM passivation studies to kilogram quantities in continuous pyrolyzers. We used a twin-screw reactor to co-feed 0.25 kg h⁻¹ of acid pretreated biomass and 10 kg h⁻¹ of steel shot heat carrier to scale-up experiments by 2500 fold.⁷³ Sugars were recovered with phenolic compounds as heavy ends while low molecular weight oxygenated compounds and water were separately collected as “light ends.” In tests with red oak, sugar yields (levoglucosan, xylosan, galactose, cellobiosan and smaller amounts of other anhydrosugars)

increased from 6% (biomass basis) to 17%. Sugar yields for switchgrass increased from 4.5% to 13% (Figure 12).

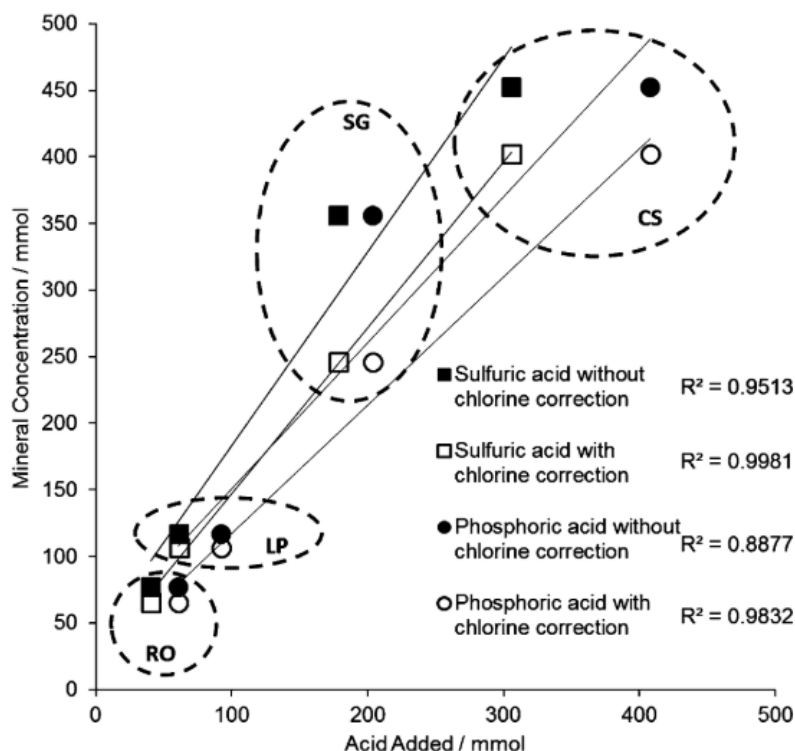


Figure 11. Correlation between total AAEM valency of biomass and optimal acid infusion to achieve maximum yield of levoglucosan from biomass pyrolysis at 500°C (RO: red oak, SG: switchgrass, CS: corn stover). Reproduced from Reference 48. Copyright 2012 Chem SusChem.

These gains in sugar were accompanied by losses in phenolic oil (pyrolytic lignin), decreasing by 49% and 14% for red oak and switchgrass, respectively. Much of this mass loss correlated with an increase in char yield. We also observed agglomeration of char produced from acid pretreated biomass (shown in Scheme 4), a problem observed by others for pyrolysis of acid infused biomass⁷⁴ and acid leached biomass.⁷⁵ We described these agglomerates as having a “vitreous lustre” with the appearance of having melted at some point.⁷³ In fact, we choose to use an auger reactor in these trials because of its ability to crush the friable agglomerates. In contrast, attempts with a fluidized bed ended prematurely with agglomerated char fouling the reactor.⁷⁶ We attribute

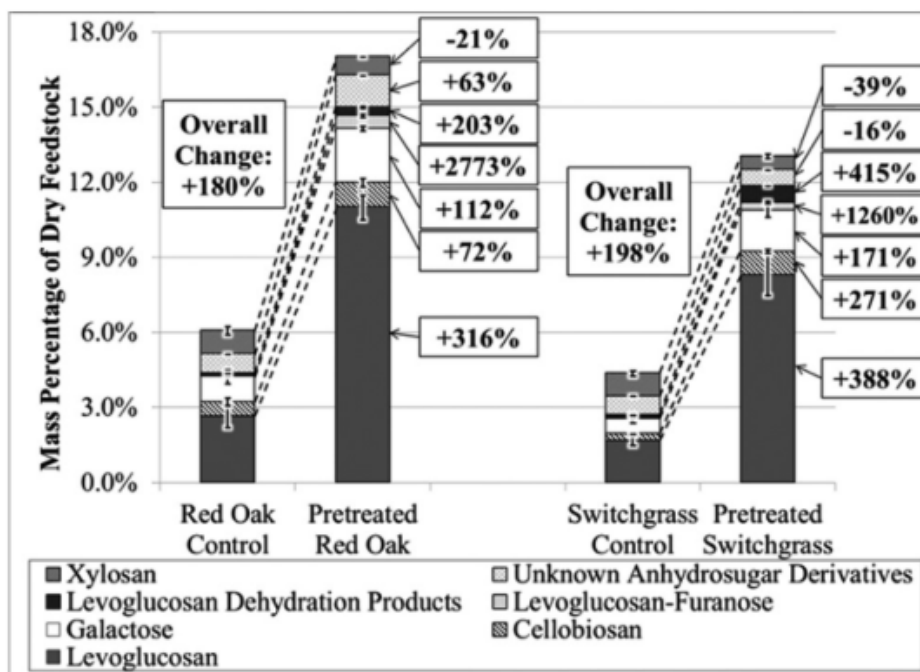
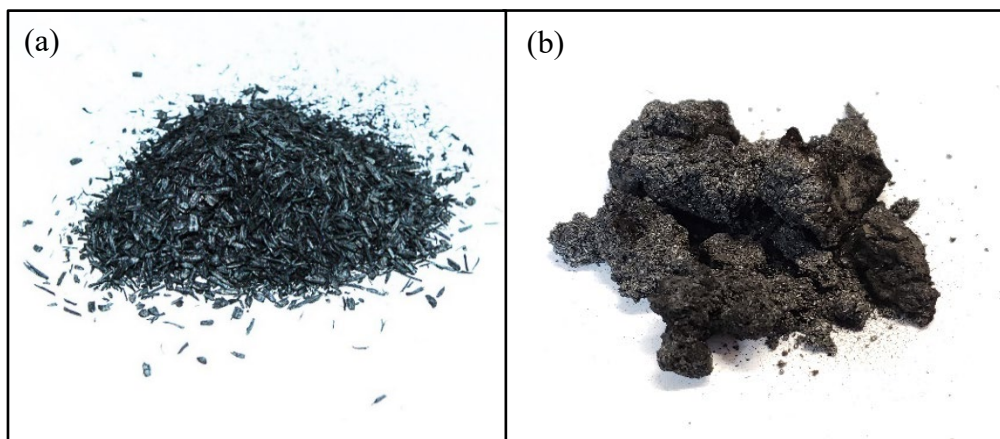


Figure 12. Sugar yields from untreated and acid pretreated red oak and switchgrass (0.4 wt% and 2.0 wt% acid infusion, respectively; pyrolysis at 500°C in auger reactor heated with steel shot). Reproduced from Reference 73. Copyright 2014 Green Chemistry.

the agglomerates to a slowing of lignin cracking to vapors and dehydration to char allowing time for the lignin to melt into cohesive masses that yield char agglomerates upon dehydration, a hypothesis inspired by the well-known phenomenon of char agglomeration during the fast pyrolysis of technical lignin.⁷⁷ However, at that time we could not dismiss the possibility that increased conversion of polysaccharides to sugar produced a melt that dehydrated to char faster than it could devolatilize.^{78–80} Indeed, cellulose has been observed to undergo a melt phase when depolymerizing.⁸¹

Even though the auger reactor was able to operate in the presence of char agglomerates, significant derating of biomass throughput nevertheless occurred, decreasing from about 1 kg h⁻¹ to only 0.25 kg h⁻¹ to assure that agglomerates were crushed at the same rate as they formed.⁸² The turbulent motion of sand in a fluidized bed is able to attrit the friable agglomerates into particles

fine enough to elutriate from the fluidized bed, but at a rate much lower than they were crushed in the auger reactor, causing greater derating of biomass throughput in a fluidized bed operated with acid infused biomass.⁸³ In principle, rates of attrition could be enhanced with more aggressive hydrodynamics⁸⁴ in a commercial-scale fluidized bed pyrolyzer, but avoiding formation of agglomerated char altogether while still enhancing sugar production is a preferable solution to the problem.



Scheme 4. Effect of acid infusion pretreatment on formation of biochar agglomerates during fluidized bed pyrolysis. (a) Biochar powder from pyrolysis of untreated red oak; (b) biochar agglomerates from pyrolysis of acid pretreated red oak. Unpublished photographs from the author's laboratory.

We first attempted to solve the agglomeration problem by admitting oxygen into the pyrolyzer, motivated by an earlier observation that small amounts of oxygen promoted lignin depolymerization and increased the porosity of the char product.⁷⁶ Although increasing amounts of oxygen (equivalence ratios of 13.5%, 27%, and 54%) reduced the amount of agglomerated char produced from acid infused red oak and improved operability of the fluidized bed, it appeared to be simply oxidizing agglomerates as they formed rather than preventing agglomeration. As with autothermal pyrolysis of untreated biomass,^{20,21} loss of bio-oil was relatively modest at low equivalence ratios although the heavy ends of bio-oil (sugar and phenolic compounds) decreased for equivalence ratios above 13.5%. Unfortunately, the effectiveness of this approach to mitigating

the problem of char agglomeration requires equivalence ratios higher than needed for autothermal operation of a pyrolyzer.

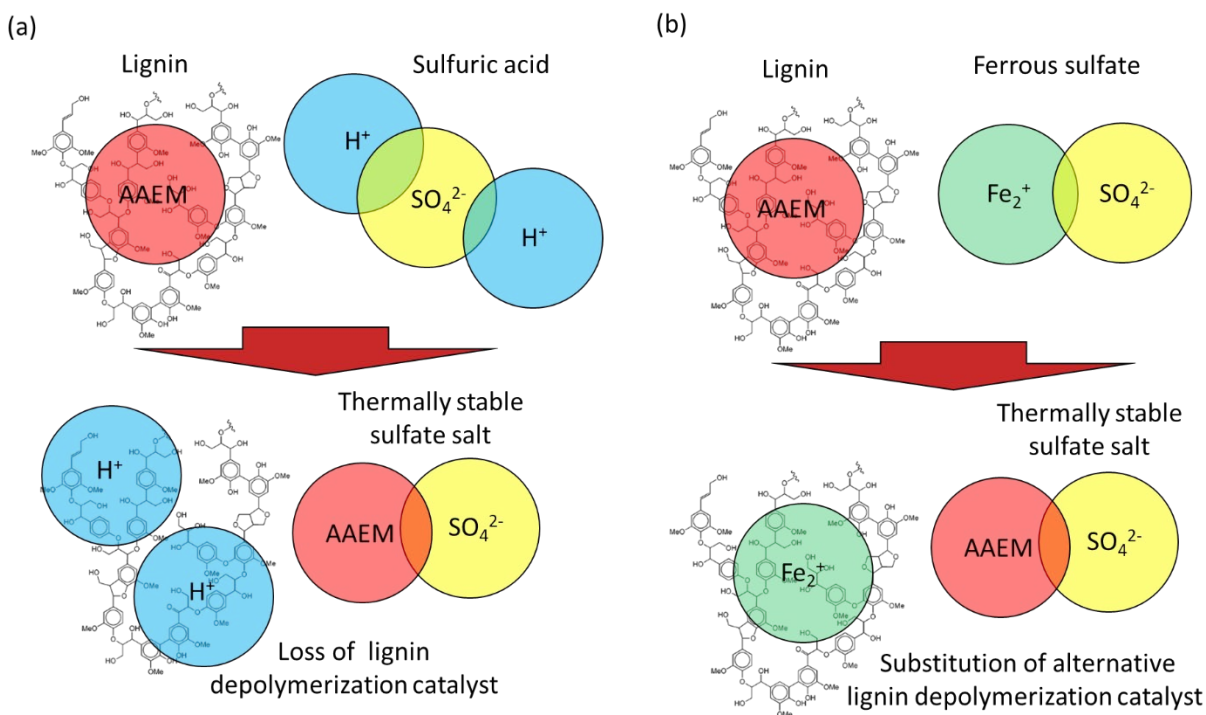
Another possibility is to combine acid infusion with another chemical pretreatment that mitigates melting of lignin. This idea was inspired by work in our laboratory to reduce char agglomeration during pyrolysis of technical lignin by mixing it with 5 wt% calcium hydroxide ($\text{Ca}(\text{OH})_2$), which produced upon pyrolysis a relatively fine powder that readily elutriated from the fluidized bed in the same manner as char from untreated biomass.⁸⁵ Microscopic examination suggested that the lignin still melted but was confined to droplets no larger than 50 μm diameter. We hypothesized that the $\text{Ca}(\text{OH})_2$ reacted with carboxylic functionality in the lignin to form cross-linked aryl-COO-CaOH. However, addition of $\text{Ca}(\text{OH})_2$ to acid-infused lignocellulosic biomass would be counter-productive to our goal of enhancing sugar production because calcium is among the alkali earth metals known to catalyze pyranose ring fragmentation.⁵⁴

In 2019, we hypothesized AAEM to be a powerful catalyst for both fragmenting pyranose rings and depolymerizing lignin. If correct, acid infusions, by converting AAEM into thermally stable salts, both promoted sugar production and char agglomeration. That is, by slowing depolymerization, lignin has time to melt, coalesce, and dehydrate to char agglomerates (see Scheme 5a).

In contrast to the extensive literature on the effect of AAEM on carbohydrate pyrolysis, surprisingly few studies have explored AAEM as a lignin depolymerization catalysts. Most relevant studies have been performed in microreactors,^{86,87} which can only analyze for monomers and a few dimers from the pyrolysis of lignin. These generally found a statistically significant increase in phenolic monomers from the presence of alkali metals, particularly potassium, but increases were modest. Studies have not been performed that directly measure depolymerization

in the condensed phase where the competition between cracking/devolatilization and melting/dehydration occurs. However, computational studies on dimer model compounds suggest that AAEM promotes lignin depolymerization through C β -O concerted decomposition.⁸⁸

Thus, we sought a pretreatment that both passivated AAEM and added an alternative lignin depolymerization catalyst that was not active toward pyranose ring fragmentation. The literature



Scheme 5. (a) Acid infused into biomass reacts with naturally occurring alkali and alkaline earth metals to form thermally stable salts. Passivation of AAEM prevents it from catalyzing pyranose ring breaking but also lignin depolymerization, the latter causing char agglomeration. (b) Ferrous sulfate infused into biomass also passivates AAEM but adds ferrous ion as lignin depolymerization catalyst, thus preventing char agglomeration while enhancing sugar production. Magnesium ions and, to a lesser extent, ammonium ions also showed catalytic activity toward lignin depolymerization.

provided little guidance with respect to catalysts suitable for depolymerizing lignin at pyrolysis temperatures. In tests with high ash feedstocks, we found ferrous and magnesium cations showed good activity as lignin depolymerization catalysts while not substantially promoting pyranose ring fragmentation (see Scheme 5b).⁸³

We ran experiments in a fluidized bed pyrolyzer operated under autothermal conditions ($ER = 0.09-0.12$) to compare pretreatments of sulfuric acid (H_2SO_4), magnesium sulfate ($MgSO_4$), and ferrous sulfate ($FeSO_4$) with untreated corn stover. Table 4 summarizes yields of heavy ends and sugars and the maximum weight hourly space velocity (WHSV) achieved in the experiments (WHSV, defined as the ratio of biomass throughput to mass of fluidized bed media, serves as a useful comparative measure of throughput). All pretreatments produced significant increases in heavy ends compared to untreated corn stover: 47%, 24% and 88% for H_2SO_4 , $MgSO_4$, and $FeSO_4$, respectively. Although heavy ends include both sugars from polysaccharides and phenolic oil from lignin, most of the gain is from increasing sugar yields, which increased 13-fold, 7-fold, and 13-fold for H_2SO_4 , $MgSO_4$, and $FeSO_4$ pretreatments, respectively. The most distinguishing feature of the $MgSO_4$, and $FeSO_4$ pretreatments was the ability to operate the fluidized bed pyrolyzer at the same WHSV as untreated corn stover ($10\ h^{-1}$) while steady operation on acid pretreated corn stover forced WHSV to be reduced to only $1\ h^{-1}$ to prevent char agglomeration from fouling and defluidizing the reactor.

Table 4. Comparison of pretreatments to enhance sugar production.⁸³

	No treatment	H_2SO_4 pretreatment	$MgSO_4$ pretreatment	$FeSO_4$ pretreatment
Heavy ends yield (wt%)	17	25	21	32
Sugar yield (wt%)	0.9 ± 0.1	11.9 ± 0.8	6.6	11.8 ± 0.7
Maximum WHSV (h^{-1})	10	1	10	10

The advantage of the new pretreatments is evident in the bubble plot of Figure 13, which plots sugar yield vs weight hourly space velocity for untreated and pretreated corn stover under both conventional pyrolysis in nitrogen and autothermal pyrolysis in air. The size of the circle designating each data point represents the volumetric sugar productivity (VSP) achieved in the test, which is proportional to the product of sugar yield Y_s and WHSV:

$$VSP = \rho_b Y_s WHSV \quad (3)$$

Untreated corn stover processed in a conventional pyrolyzer only achieved VSP of $62 \text{ g L}^{-1}\text{h}^{-1}$. Autothermal pyrolysis, by increasing WHSV by a factor of 2.5, increased VSP to $157 \text{ g L}^{-1}\text{h}^{-1}$. Autothermal pyrolysis of sulfuric acid pretreated corn stover, while increasing sugar yield from 0.9 wt% to 12 wt% could only operate at WHSV of 1.0 h^{-1} , resulting in a relatively modest increase in VSP to $206 \text{ g L}^{-1}\text{h}^{-1}$. However, by avoiding char agglomeration, the new pretreatments allowed autothermal pyrolysis with both high sugar yield and WHSV resulting in VSP of $1,194 \text{ g L}^{-1}\text{h}^{-1}$ and $2,041 \text{ g L}^{-1}\text{h}^{-1}$ for MgSO_4 and FeSO_4 pretreated corn stover, respectively. The VSP for FeSO_4 is 10 times higher than achieved for pyrolysis of acid pretreated corn stover and more than 400 times higher than typical for enzymatic hydrolysis.⁸³

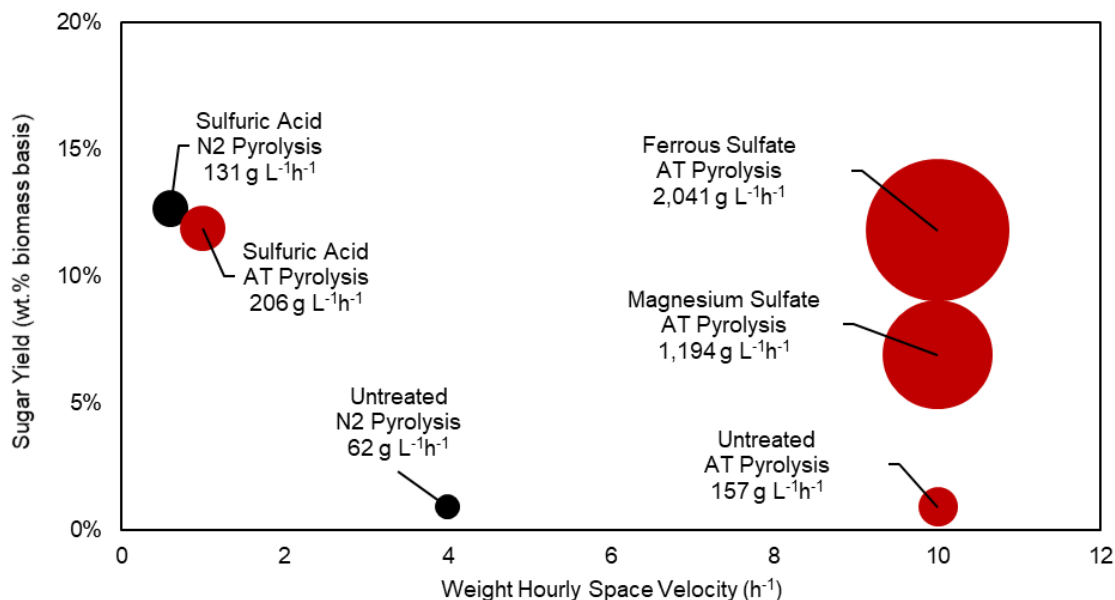


Figure 13. Comparison volumetric sugar productivity for different pretreatments of corn stover pyrolyzed at maximum sustainable feed rate under conventional (N₂) and autothermal (AT) operating conditions. Reproduced from Reference 83. Copyright 2020 Chemical Engineering Journal.

Another advantage FeSO_4 pretreatment is the absence of an optimal pretreatment level, which was very prominent for acid pretreatment.⁴⁸ Addition of acid beyond what was necessary to passivate AAEM promoted acid-catalyzed dehydration of cellulose to furans, reducing sugar yields. In practice, the ash content of biomass feedstock is likely to vary widely during pretreatment, making it difficult if not impossible to consistently pretreat at the optimal acid level. Because the ferrous cation catalyzes lignin depolymerization without affecting polysaccharide chemistry, sugar yield increases monotonically with increasing FeSO_4 pretreatment until it plateaus upon reacting with all the AAEM in the biomass.⁸³ Thus, to maximize sugar yields it is only necessary to pretreat with FeSO_4 at a level appropriate to the highest AAEM concentrations expected in the feedstock.

BIO-OIL FRACTIONATION

Production of pyrolytic sugars will require innovations in bio-oil recovery. Traditionally, pyrolytic vapors are rapidly cooled by direct contact with a non-polar liquid such as hydrocarbons. Rapid cooling is important to prevent secondary reactions that might otherwise decompose valuable bio-oil components, including sugars.⁸⁹ Use of a non-polar liquid to quench vapors facilitates separation of the largely polar products of pyrolysis.⁹⁰ However, this one-pot recovery of condensable organic compounds results in bio-oil consisting of an emulsion of lignin-derived compounds in an aqueous phase of mostly carbohydrate-derived compounds.⁹¹ Although the emulsion phase (so-called pyrolytic lignin) can be precipitated from the aqueous phase by addition of water to the bio-oil, the sugar is dissolved in the aqueous phase along with literally hundreds of other water-soluble compounds including aldehydes, ketones, carboxylic acids, alcohols, esters, and phenolic monomers. Recovering the sugar from this solution is problematic.

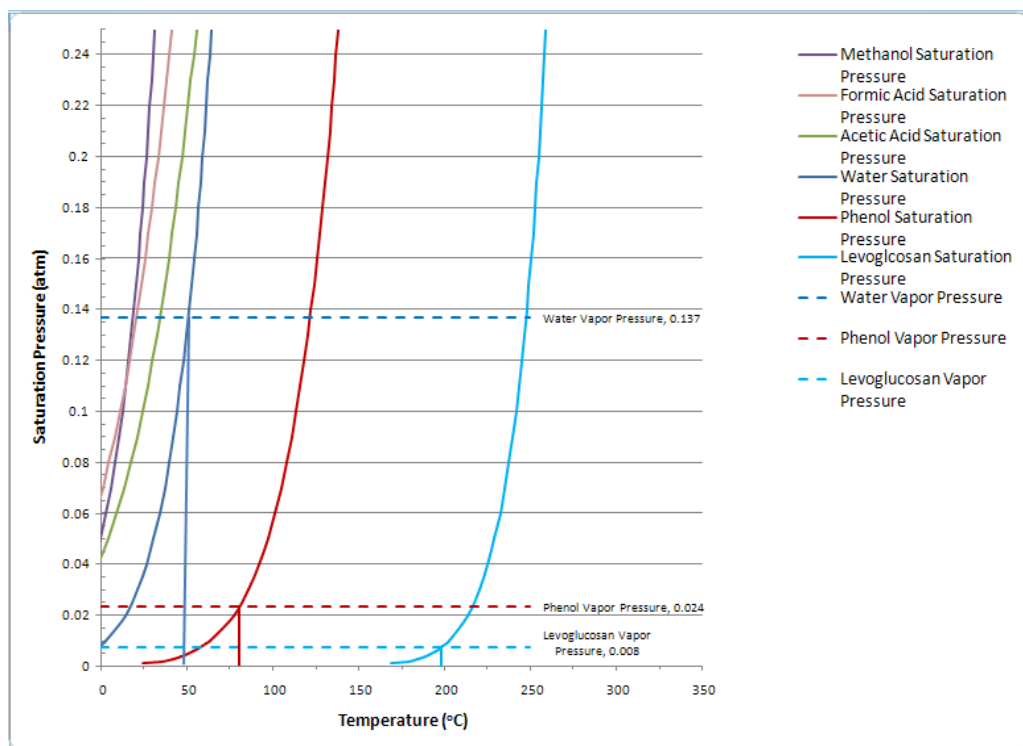
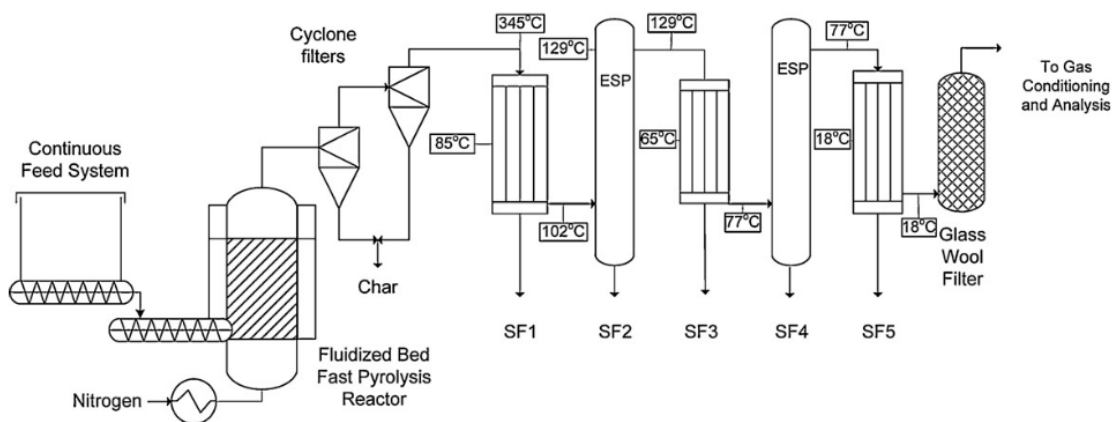


Figure 14. Differences in condensation temperature among representative vapor products of fast pyrolysis. Reproduced from Reference 93. Copyright 2012 Journal of Analytical and Applied Pyrolysis.

Although boiling points of the compounds found in bio-oil range between -19°C to over 385°C ,⁹⁰ distillation of bio-oil to separate them is not practical because of the reactive nature of the bio-oil.⁹² To overcome this problem we began exploring about a decade ago the possibility of selectively condensing compounds from the pyrolysis product stream as heavy, middle, and light fractions of bio-oil. As illustrated in Figure 14, the in-stream partial pressures of many bio-oil compounds intersect their corresponding saturation pressure-temperature curves at widely separated temperatures, suggesting the possibility of staged condensation.⁹³ The original apparatus, illustrated in Scheme 6, was based on pairing a temperature-controlled indirect contact heat exchanger to condense vapors at a prescribed temperature with an electrostatic precipitator (ESP) to collect any aerosols generated in the cooled gas stream.⁹³ Stage fraction 1 (SF1) cooled the pyrolysis vapor stream to 102°C and condenses so-called heavy ends on the wall of the heat

exchanger while SF2 collected aerosolized heavy ends. SF 3 and 4 cooled the stream to 77°C and condensed vapors and collected aerosols of intermediate boiling point compounds referred to as the middle fraction. SF5 was a heat exchanger that cooled the stream to 18°C and collected an aqueous phase known as light ends. A simple glass wool filter at the end of the fractionation system protected downstream analytical instrumentation from any residual aerosols (eventually this filter was replaced with an ESP to improve mass balances). Depending upon pyrolysis temperature, heavy ends (SF 1 and SF 2), middle fraction (SF 3 and SF 4), and the light ends (SF 5) constituted approximately 50%, 10%, and 40% of the liquid product although SF 5 consisted of about 90% water.⁹⁴ As suspected, over 85% of water-soluble sugars and virtually all of the levoglucosan was collected in SF 1 and SF2. Similarly, 97% of water insoluble phenolic oligomers (pyrolytic lignin) was recovered in SF 1 and 2. The intention was for SF 3 and SF 4 to concentrate phenolic monomers but other than a tendency to collect phenol (the properties of which were used to design these two stage fractions) and alkylated phenols, phenolic monomers were distributed in all the stage fractions.



Scheme 6. Fractionating bio-oil recovery system developed at Iowa State University. Heavy ends are recovered in SF 1 and SF 2; a middle fraction is recovered in SF 3 and SF 4 and light ends are recovered in SF 5. Reproduced from Reference 93. Copyright 2012 Journal of Analytical and Applied Pyrolysis.

About the same time Westerhof et al.⁹⁵ developed a bio-oil recovery system also based on a series of temperature-controlled condensers to concentrate classes of compounds according to molecular weight, although they did not employ ESPs to capture aerosols. We found that more than half of the heavy ends were recovered as aerosols in the ESP instead of condensing on the cold walls of the heat exchange surfaces.⁹³ Other researchers have subsequently incorporated similar condensers in their bio-oil recovery systems.^{96–98} A notable innovation in selective condensation was achieved by Linfors et al.⁹⁹ at VTT Technical Research Centre of Finland who employed white oil as coolant in a temperature-controlled direct contact heat exchanger (quench vessel) followed by an ESP to recover heavy ends in two stages.

The VTT temperature controlled quench vessel⁹⁹ helped inspire our recent replacement of the first indirect contact heat exchanger (SF 1) in our bio-oil recovery system with a novel direct contact heat exchanger that injects a fine stream of cold water in counterflow to the hot vapor stream from the pyrolyzer.¹⁰⁰ Like the injection of chilled white oil into the VTT quench vessel, this scheme has the advantage of rapidly cooling the whole vapor stream rather than just the vapors in the boundary layer near the cooled wall of the direct contact heat exchanger. Laboratory-scale experiments demonstrated that direct contact heat exchange improved sugar yield by limiting exposure of condensed liquids (whether films on heat exchanger surfaces or aerosols in the pyrolysis gas stream) to the core flow of hot gases in an indirect contact heat exchanger.¹⁰⁰ However, rather than condensing the pyrolysis vapors into a liquid water stream, the temperature of the quench vessel was held at 125°C, just above the dew point of water but well below the dew point of levoglucosan. As a result, the water flashed to steam as it cooled hot vapors, its enthalpy of evaporation removing heat from condensing heavy ends (SF 2 remained an ESP to collect heavy ends aerosols).

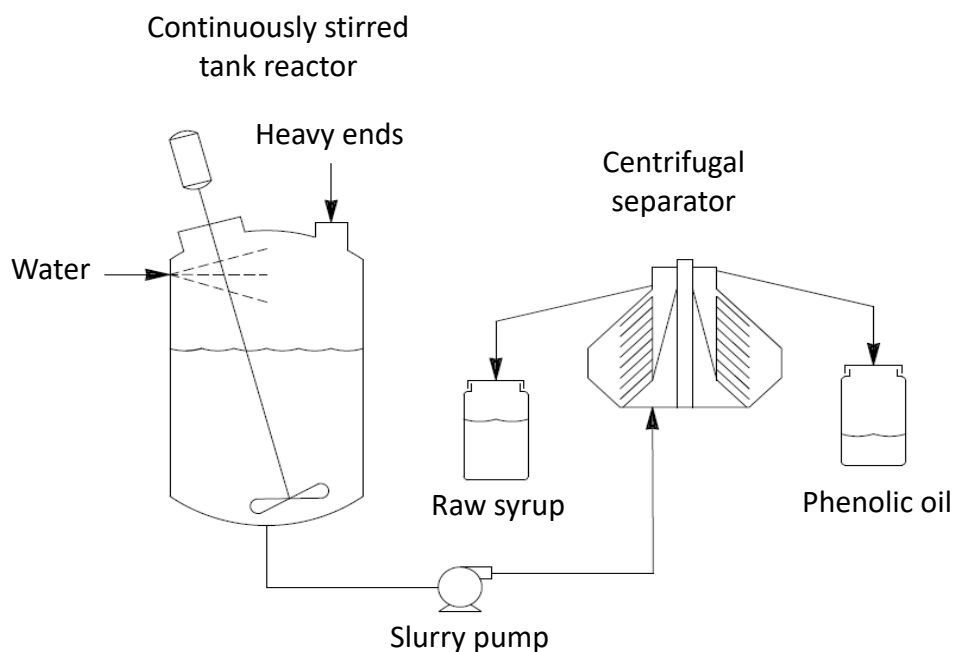
This scheme increased heavy ends yield by 13% and essentially eliminated fouling associated with polymerization and dehydration of sugars condensed on surfaces of the indirect heat exchanger employed as SF 1 in our original fractionating bio-oil recovery system. In principle, the injected water increases electrical load on the chiller used to provide coolant to SF 5 and SF 6, where the aqueous phase of bio-oil is recovered. In practice, the amount of water injected into SF 1 was a small fraction of product water and thus did not substantially add to the chiller load on downstream condensers. Furthermore, we anticipate that the organic content of the aqueous phase, consisting of light oxygenated organic compounds, is of such little value that commercial plants would not even condense it but rather route it with the non-condensable gases to a “tail gas” burner, providing heat to dry biomass feedstock.

SUGAR RECOVERY AND PURIFICATION

Whereas sugars in conventional bio-oil recovery end up with other water-soluble compounds in the aqueous phase, sugars in our fractionating bio-oil recovery system appear in the heavy ends fraction along with water-insoluble phenolic compounds. We use liquid-liquid extraction to produce a sugar-rich aqueous extract, referred to as syrup, and a phenolic oligomer-rich raffinate, referred to as phenolic oil.¹⁰¹ A single extraction using a 1:1 mass ratio of water to heavy ends removed about 80% of the sugar while two consecutive extractions recovered over 93% of the sugars from SF1 and SF2 in this unoptimized process.

We have developed this sugar extraction process into a pilot-scale system for continuous separation of heavy ends into syrup and phenolic oil streams (Scheme 7), which has been coupled to the fractionating bio-oil recovery of our fast pyrolysis pilot plant. Heavy ends from SF1 (quench spray tower) and SF2 (ESP) of the bio-oil recovery system flow into a temperature controlled,

continuously stirred tank along with a continuous stream of water. Extraction time is controlled through monitoring the speed of the discharge pump at the exit of the tank. The discharged mixture of sugar-rich syrup and phenolic oil enters a continuous centrifugal separator, whose performance is controlled through choice of interchangeable weir plates, rotational speed, and separation temperature. This continuous system has successfully extracted almost 98% of the sugars in the heavy ends into the syrup stream. The composition of the extract (syrup) and raffinate (phenolic oil) is detailed in Figure 15. Sugars constitute 74% of the syrup (dry basis) while phenolic compounds make up 60% of the phenolic oil (dry basis).



Scheme 7. Schematic of pilot-scale process for continuous liquid-liquid extraction of sugars from the heavy ends of bio-oil as raw syrup and phenolic oil (unpublished drawing the author's laboratory).

The syrup from both laboratory and pilot-scale extraction tests are contaminated with organic compounds other than sugars including carboxylic acids, furans, and phenolic monomers, which we have found to be inhibitory to different extents toward the growth of ethanologenic *E. coli* engineered to use levoglucosan as its sole energy and carbon source.¹⁰¹ Table 5 details the

contaminants found in the syrups produced from pyrolysis of a variety of biomass feedstocks (without pretreatment).¹⁰² If intended for fermentation, this pyrolytic syrup will require some degree of purification to remove the inhibitory compounds.^{101–103} As shown in Figure 15, phenolic compounds make up 77% of these non-sugar constituents of the syrup (unpublished data from our laboratory). Their removal became the focus of our subsequent efforts to purify pyrolytic sugars.

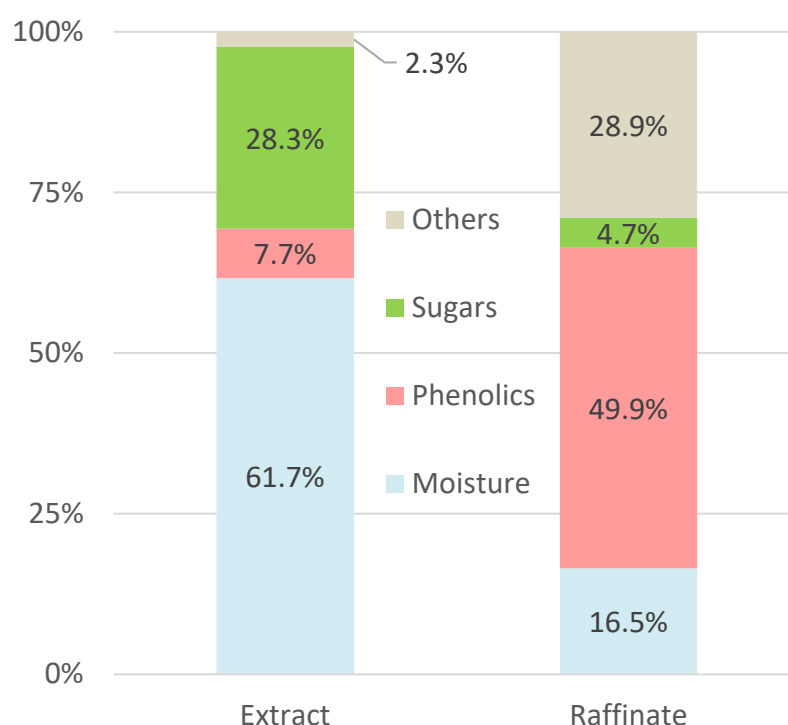


Figure 15. Composition of extract (syrup) and raffinate (phenolic oil) from on-line liquid-liquid extraction of sugars from heavy ends of bio-oil produced from autothermal pyrolysis of (untreated) red oak. Unpublished data from the author's laboratory.

Table 5. Abundance (wt%) of identified non-sugar compounds in syrup from liquid-liquid extraction of the heavy ends of bio-oil.¹⁰²

	Switchgrass	Corn stover	Red oak	Poplar	Pine
Furans					
furan	0	0	0	0.57±0.02	0.500±0.009
2-furaldehyde	0	0.526±0.003	0	0.540±0.006	0.507±0.003
2-furanmethanol	0	0.32±0.01	0.260±0.002	0.62±0.06	0.50±0.02
5-hydroxymethylfurfural	0.549±0.004	0.74±0.04	0.60±0.02	0.675±0.008	0.77±0.04
Total furans	0.549±0.004 ^a	1.58±0.04 ^b	0.86±0.02 ^c	2.41±0.06 ^d	2.28±0.05 ^d
Aromatic Hydrocarbons					
ethylbenzene	0	0.02±0.01	0	0.027±0.009	0.020±0.003
p-/m-xylene composite	0	0.015±0.002	0	0.054±0.003	0.003±0.000
styrene	0	0.017±0.000	0	0.024±0.002	0.017±0.000
Total aromatic hydrocarbons	0.000 ^a	0.05±0.01 ^b	0.000 ^a	0.11±0.01 ^c	0.040±0.003 ^b
Anisoles					
anisole	0	0	0	0.008±0.002	0
2-methylanisole	0	0.01±0.01	0	0.115±0.007	0.067±0.004
vinylanisole	0	0	0	0.011±0.000	0.011±0.000
Total anisoles	0.000 ^a	0.01±0.01 ^a	0.000 ^a	0.134±0.007 ^b	0.078±0.004 ^c
Phenols					
phenol	0	0	0	0.018±0.004	0
o-cresol	0	0	0	0.006±0.000	0.009±0.002
2,6-dimethylphenol	0.004±0.002	0.014±0.003	0.007±0.002	0.020±0.003	0.030±0.002
m-cresol	0	0	0	0.004±0.002	0.006±0.005
2,4-dimethylphenol	0.046±0.003	0.041±0.002	0.009±0.003	0.075±0.004	0.08±0.01
3,5-dimethylphenol	0	0.004±0.002	0	0	0.008±0.002
4-ethylphenol	0.001±0.002	0.010±0.002	0.002±0.002	0.011±0.005	0.012±0.002
3-ethylphenol	0	0	0.002±0.003	0.009±0.002	0.014±0.000
3,4-dimethylphenol	0	0	0	0.0009±0.002	0.0019±0.002
3-ethyl-5-methylphenol	0.031±0.005	0.06±0.01	0	0	0.03±0.05
Total phenols	0.082±0.006 ^a	0.13±0.01 ^b	0.020±0.005 ^c	0.152±0.009 ^b	0.21±0.06 ^{a,b,c}
Guaiacols					
2-methoxy-4-methylphenol	0.018±0.003	0.06±0.01	0.023±0.006	0.125±0.009	0.14±0.01
4-ethyl-2-methoxyphenol	0	0	0	0.001±0.002	0.002±0.002
2-methoxy-4-propylphenol	0	0	0	0.003±0.000	0.006±0.000
isoeugenol	0.019±0.006	0.016±0.004	0.012±0.004	0.048±0.003	0.16±0.02
coniferaldehyde	0.006±0.000	0.006±0.000	0.07±0.02	0.085±0.008	0.015±0.002
Total guaiacols	0.043±0.007 ^a	0.08±0.01 ^a	0.11±0.02 ^a	0.26±0.01 ^b	0.32±0.02 ^b
Syringols					
4-methyl-2,6-dimethoxyphenol	0	0.005±0.002	0.075±0.004	0.102±0.009	0
Miscellaneous Aromatics					
2,3-dimethoxytoluene	0	0	0	0.011±0.000	0.010±0.002
3,4-dimethoxytoluene	0.003±0.003	0.009±0.000	0.008±0.002	0.021±0.004	0.013±0.002
1,2,4-trimethoxybenzene	0.003±0.000	0.014±0.003	0.004±0.002	0.013±0.002	0.016±0.003
hydroquinone	0.041±0.004	0.056±0.009	0.045±0.009	0.070±0.007	0.042±0.006
1,3-benzenediol (resorcinol)	0.022±0.002	0.024±0.002	0.024±0.002	0.024±0.002	0.025±0.002
1,2-benzenedimethanol	0.055±0.004	0.069±0.004	0.064±0.004	0.074±0.003	0.10±0.01
2,5-dimethoxybenzylalcohol	0	0.014±0.000	0.039±0.003	0.052±0.003	0.054±0.008
4'-hydroxy-3'-methoxyacetophenone	0.018±0.002	0.021±0.002	0.028±0.003	0.057±0.005	0.11±0.02
3,4-dimethoxyacetophenone	0.007±0.002	0.013±0.002	0.009±0.002	0.019±0.002	0.009±0.003
guaiacyl acetone	0.013±0.002	0.017±0.003	0.025±0.003	0.044±0.003	0.08±0.01
3',5'-dimethoxy-4'-hydroxyacetophenone	0.055±0.002	0.066±0.003	0.09±0.01	0.110±0.004	0
Total misc. aromatics	0.217±0.008 ^a	0.30±0.01 ^b	0.34±0.02 ^b	0.50±0.01 ^c	0.46±0.03 ^c
Unclassified					
methylcyclopentenolone	0.152±0.004	0.21±0.01	0.162±0.006	0.241±0.004	0.234±0.009

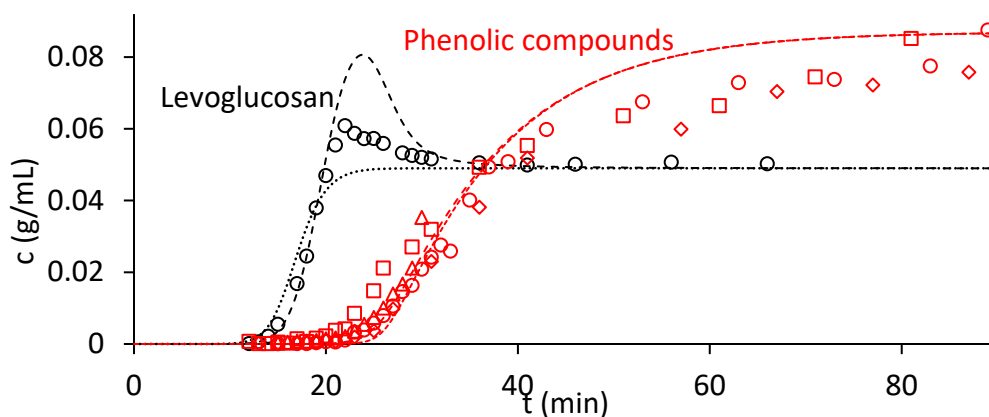
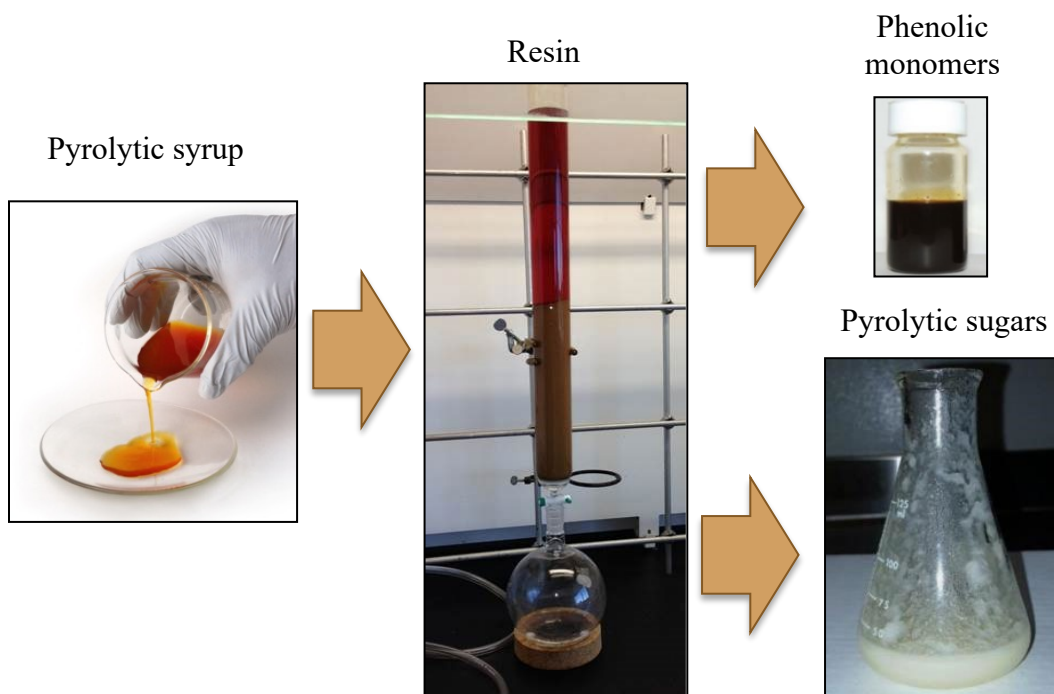


Figure 16. Comparison of elution of phenolics and levoglucosan from resin column. Experimental levoglucosan (\circ) and phenolic species (run 1 = \circ ; run 2 = \square ; run 3 = \diamond ; run 4 = \triangle) for SP207 resin packed column. Computed elution curves for single component (\cdots) and competitive ($--$) Langmuir isotherms. Reproduced from Reference 57. Copyright 2018 Separation and Purification Technology.

Our earliest efforts to produce clean pyrolytic sugars employed ligninolytic enzymes,¹⁰⁴ overliming,¹⁰³ liquid-liquid extraction, ionic liquids, and ion exchange resins.¹⁰² More recently, we have identified hydrophobic polymeric resins as low cost and regenerable adsorbents for removing phenolic compounds along with other contaminants in pyrolytic syrups.⁵⁷ Specifically, we employed Sepabeads resin SP207 (Mitsubishi Chemical) and Amberlite XAD4 resin (Rohm and Haas), which have previously been used to recover phenolic compounds from winery wastes (also a sugar-rich liquid).¹⁰⁵ In detailed equilibrium and kinetic adsorption studies we found an order of magnitude greater mass adsorption capacity for phenolic species compared to levoglucosan for mixtures of these compounds although the kinetics of adsorption were approximately an order of magnitude slower for phenolic species versus levoglucosan.⁵⁷ This data was applied to an equilibrium-dispersive model for column chromatography, which showed good agreement with our experimental column data (see Figure 16). The appearance of the raw pyrolytic syrup before filtration and the resulting mixed sugars and phenolic monomers after resin filtration (and evaporation of cleaned syrup to precipitate sugars) are shown in Scheme 8. The raw syrup has a

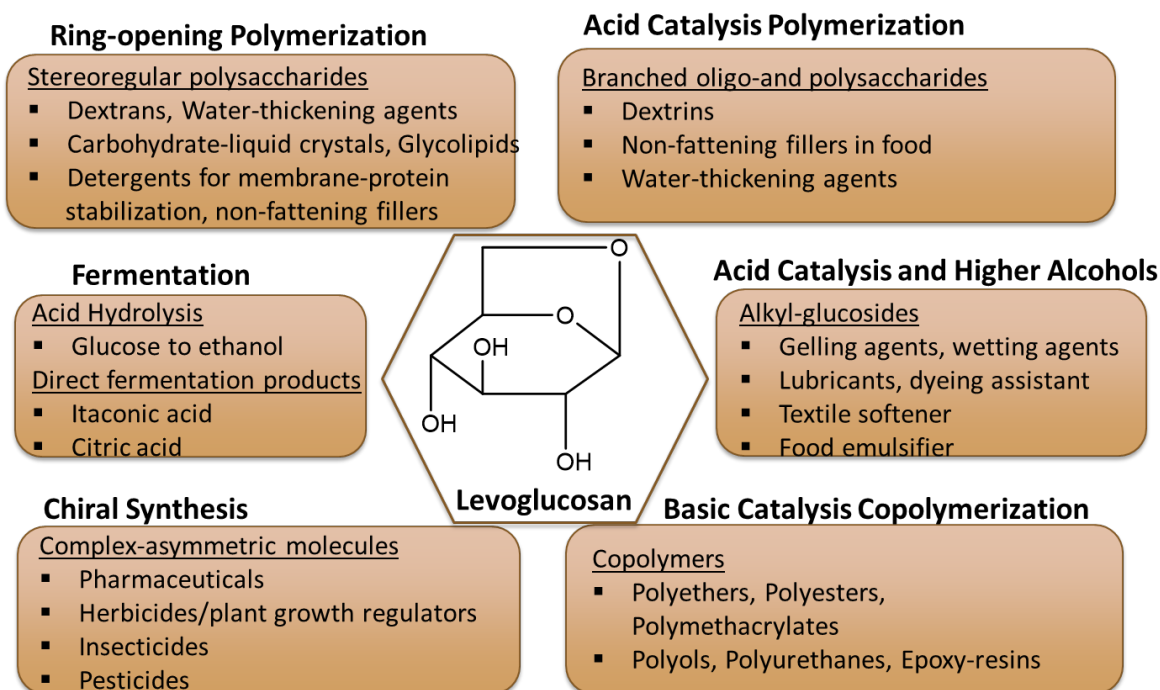
distinct reddish hue from the phenolic content, the purified sugars are brilliant white, and the separated phenolic monomers have a dark amber color. We are currently adapting the process to a small pilot-scale simulated moving bed to provide a continuous process of sugar purification.



Scheme 8. Use of hydrophobic polymeric resins in single column breakthrough studies to separate pyrolytic syrup into pyrolytic sugars and phenolic monomers. Unpublished photographs from the author's laboratory.

The purified sugar is a mixture of levoglucosan, mannose, xylose, galactose and cellobiosan.⁵⁷ Hydrolysis of this mixture yields glucose and xylose,¹⁰⁶ which could be fermented with appropriate microorganisms and is the approach most other researchers have taken in utilizing pyrolytic sugars, as reviewed by Jiang et al.¹⁰⁷ Considering the low-cost of dextrose from starch crops, a better strategy might be recovery and purification of the levoglucosan, representing around 60% of the sugars in the syrup, for use in synthesis of products not otherwise accessible from dextrin. A review by de Wild¹⁰⁸ notes that such products include co-polymers, detergents, lubricants, pesticides, and pharmaceuticals among others (see Scheme 9).

We have recently developed a process for recovering pure levoglucosan from the heavy ends of bio-oil (Scheme 10). After liquid-liquid extraction of sugar rich solution (syrup) from the heavy ends of bio-oil and filtering phenolics and other non-sugar components from the syrup, the cleaned syrup (referred to as clarified juice in analogy with the name of the sugar stream at a similar point in a cane sugar refinery) is subjected to evaporation and concentration into a “mother liquor” at which point sugars crystals precipitate as a separate phase. This mixture of sugar crystals and mother liquor is filtered and washed with cold methanol, which leaves behind very pure ($102.5\% \pm 3.109\%$) levoglucosan. Although the spent mother liquor still contains most of the original levoglucosan, the process could be optimized to recover more of it through multi-stage crystallization, as practiced in the sugar industry. Nevertheless, even at modest levoglucosan recovery an economic analysis indicates levoglucosan could be produced at \$1333 per MT, which is one-tenth the current market price for levoglucosan synthesized from glucose.¹⁰⁹

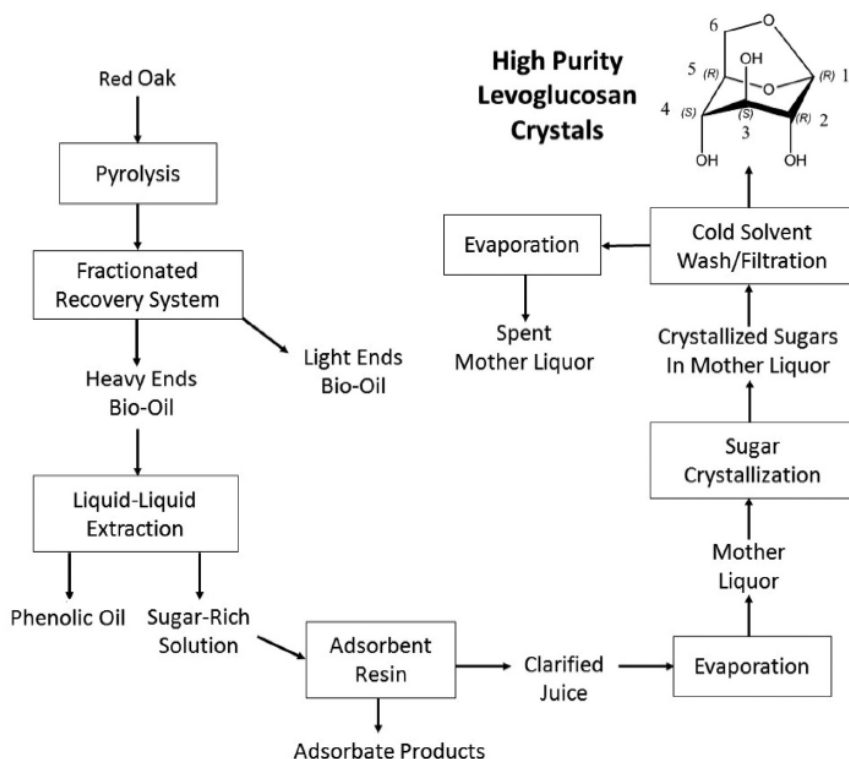


Scheme 9. Potential products from levoglucosan.¹⁰⁸

OUTLOOK

Autothermal processing improves the technical feasibility of fast pyrolysis by eliminating ancillary heat transfer equipment, simplifying reactor operation, and intensifying the process. Enhancing sugar yields from pyrolysis of cellulosic biomass and adopting fractionating bio-oil recovery improves commercial prospects for pyrolysis by expanding and valorizing products from pyrolysis. Despite progress in developing these three technologies, commercial prospects could be improved through further research and development. Prominent opportunities are outlined below.

Char oxidation serves as the primary source of energy to autothermally heat a pyrolyzer. Our research^{20,21} suggests that around half of the energy for autothermal pyrolysis comes from char oxidation, but partial oxidation of heavy ends (sugars and phenolic oil) and light ends also



Scheme 10. Flow diagram of process developed at Iowa State University to purify levoglucosan from the products of fast pyrolysis. Reproduced from Reference 109. Copyright 2019 Green Chemistry.

contribute. Although char has interesting prospects as soil amendment and carbon sequestration agent,¹¹⁰ it currently is one of the lowest value products of pyrolysis,¹¹¹ making it the most logical source of energy to drive pyrolysis. The light ends, heavily diluted with water, is also a low value product, but the short residence time of these vapors in the reactor (typically a few seconds) makes it difficult to harness their oxidation within the pyrolyzer. Success in preferentially oxidizing char is dependent on maximizing its residence time in the presence of oxygen while minimizing residence time of vapor products. The residence time of char is a function of the size of the biomass particles from which it is produced, its friability towards breaking into fine particulate matter, the attritive environment of the fluidized bed (a function of bed media properties and reactor hydrodynamics), and the fluidization velocity.⁸⁴ One can envision a reactor designed to devolatilize biomass in an oxygen-starved zone followed by rapid transport of pyrolysis vapors out of the reactor and extended dwell time of biochar in an oxygen-rich zone.

Maximize bio-oil yield from pretreated biomass under autothermal pyrolysis. Maximizing bio-oil yield requires fully devolatilizing biomass while avoiding secondary reactions that can crack or oxidize volatile products to less desirable lighter compounds. Although devolatilization of biomass under ideal conditions is less than 1 s,¹¹² under conditions more representative of real pyrolyzers, it can take 40 s or more to fully devolatilize biomass.¹¹³ Similarly, vapor residence times in pyrolyzers are typically just a few seconds, which should minimize secondary reactions,⁸⁹ but the presence of char in the reactor can catalyze gas-solid cracking and oxidation reactions destructive to bio-oil yields.¹¹⁴ Our measurements of mass loadings of corn stover-derived biochar in fluidized bed pyrolyzers under autothermal operation indicate biochar residence times of 15-30 minutes.²¹ Although this would suggest sufficient time to completely devolatilize biomass, proximate analysis of biochar generated in the same study found that up to 20% of this solid residue

was volatile matter.²¹ Again, a reactor designed to devolatilize biomass in an oxygen-lean zone followed by submersion in an oxygen rich zone is indicated with further provision for the devolatilization to occur over several minutes.

Catalyze oxidation of char to CO₂ instead of CO to minimize the amount of char consumed in support of autothermal operation. Our research⁴⁰ has shown that AAEM in biochar catalyzes the direct production of CO₂ instead of the usual gas-solid reaction of carbon and oxygen to form CO, reducing the equivalence ratio and amount of biochar consumed to support autothermal operation of a pyrolyzer. This advantage is lost upon passivating the catalytic activity of AAEM for the purpose of enhancing sugar yields. Just as we have been able to replace passivated AAEM with ferrous cations to restore catalytic depolymerization of lignin,⁸³ it might be possible to restore catalytic oxidation of biochar by substituting an alternative catalyst. Interestingly, transition metals, which include iron, are known to be oxidation catalysts.¹¹⁵ The possibility that the same ferrous sulfate pretreatment that enhances sugar yields and catalyzes lignin depolymerization could also catalyze direct oxidation of char to CO₂ is an intriguing hypothesis. Although not yet formally tested, we found that iron-rich biochar removed from a conventional (oxygen-starved) pyrolyzer while still hot was pyrophoric, spontaneously combusting upon exposure to air, something not observed for biochar produced from untreated biomass.⁸³

Further improvements in sugar yields. Pretreatments of cellulosic biomass prior to continuous pyrolysis increases yields of sugars several fold.^{73,83} In carefully controlled micropyrolysis trials of pretreated biomass, yields have even approached that for pyrolysis of pure cellulose.⁴⁸ However, the maximum yield of levoglucosan from thermal depolymerization of pure cellulose reported in the literature is only about 60%,⁴⁹ far short of the 70-90% achieved from acid or enzymatic hydrolysis. Accordingly, a biorefinery based on pyrolysis would have to process 17-50% more

biomass than a biorefinery based on hydrolysis to achieve the same cellulosic sugar output. Carbohydrate not thermally depolymerized to sugars ends up as a mixed stream of aldehydes, ketones and furans in water,⁴⁸ likely requiring disposal and further reducing economic feasibility of a pyrolysis biorefinery. Yields of xylose from hemicellulose are even lower.¹¹⁶ Improving selectivity of pyrolysis toward sugars would be an important contribution to the field. Despite advances in understanding thermal depolymerization, it is not clear how the rate of end-chain unzipping to produce anhydrosugars can be increased relative to ring fragmentation.²⁸ A recent suggestion is that homolytic cleavage favoring levoglucosan formation can be promoted over concerted reactions through radical-generating non-thermal plasma pretreatment of cellulose.¹¹⁷ Density functional theory (DFT) applied to the pyrolysis of glucose in the presence of sodium ions indicates that AAEM increase the rates of most elementary reactions associated with the process, including the formation of levoglucosan although the rate coefficient of ring opening remains greater than this more desirable reaction.⁶³ The reaction network for pyrolysis of cellulose is so complex it is not clear whether computational modeling is sufficiently advanced to provide guidance in selecting reaction conditions or catalysts that favor sugar formation, but it is a tantalizing possibility.

Improved fractionation of pyrolysis vapors. Fractionating bio-oil recovery has made possible the separation of sugars from most of the other water-soluble products of pyrolysis,¹⁰¹ an important advance for their economic recovery. However, the technology is not sufficiently refined to segregate the sugars from phenolic monomers, which are partially water-soluble, resulting in their contamination of the raw syrup recovered from liquid-liquid extraction of the heavy ends of bio-oil. Although phenolic monomers have been efficiently removed from the syrup using resin columns,⁵⁷ their relatively heavy loading (several percent concentration in the raw syrup), adds

significantly to the expense of sugar recovery.¹⁰⁹ Referring back to Figure 14, the in-stream partial pressure of phenol (representative of phenolic monomers) intersects its corresponding saturation pressure-temperature curve at a temperature almost 250°C lower than for levoglucosan, suggesting that phenols and levoglucosan should be readily separated by selective condensation from the pyrolysis vapors stream. To date, this has not been fully exploited because of concerns that exposure of liquid levoglucosan to hot pyrolysis vapors will lead to oligomerization and dehydration,^{78–80} fouling the condenser with coke-like deposits.¹¹⁸ However, the use of temperature controlled quench reactors, whether with non-polar liquids⁹⁹ or water,¹⁰⁰ should allow tighter cuts of heavy products, reducing the amount to be removed during sugar cleaning. On the other hand, selective recovery of light oxygenates is problematic. Not only are their condensation temperatures similar, but water condenses before them, adsorbing these hydrophilic molecules to produce an aqueous solution. Another approach to their recovery would adsorb them from the vapor phase using a fixed bed operated above the dew point temperature of water. Zhang et al.¹¹⁹ explored this possibility for recovery of carboxylic acids on metal oxides. Although not tested with pyrolysis vapors, other adsorbents appropriate to removing polar vapors are also available.¹²⁰

Continuous recovery and purification of sugars from pyrolysis of cellulosic biomass. If proposed improvements to vapor-phase fractionation of pyrolysis products are unable to fully segregate phenolic monomers from the heavy ends of bio-oil, then unit operations downstream of bio-oil recovery will be needed to produce pure sugars. For example, liquid-liquid extraction of sugars from the heavy ends as currently practiced in our laboratory appears to produce raw syrup saturated with partially water-soluble phenolic monomers.⁵⁷ Use of a non-polar solvent such as toluene to extract phenolic monomers ahead of sugar recovery might reduce their burden on downstream sugar purification.¹²¹ Liquid-liquid extraction of sugars might also be optimized

through control of temperature, mixing rate, and extraction time. The use of resins to purify the raw syrup could also be optimized, as work to date has employed single passes through resin columns.¹⁰⁹ We are developing an eight-column, simulated moving bed pilot plant to continuously remove contaminants and achieve sugar purity greater than 99.9%.

Evaluating economic performance of biorefineries based on autothermal pyrolysis of pretreated biomass to produce sugars and other high value products. In the past decade, we have published studies on the economic performance of a wide range of thermochemical technologies,¹²² including three that included sugars among the projected pyrolysis products.^{69,109,123} To date none have evaluated the impact of autothermal pyrolysis on economic feasibility. Technoeconomic analyses that combined autothermal pyrolysis, biomass pretreatment to enhance sugar yields, fractionating bio-oil recovery, and sugar purification will be important to informing future research directions and advancing commercialization of pyrolysis refineries based on these technologies.

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ABBREVIATIONS

AAEM, alkali and alkaline earth metals; ESP, electrostatic precipitator; MT, metric ton; VSP, volumetric sugar productivity; WHSV, weight hourly space velocity.

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